



# Review and future trends of solar adsorption refrigeration systems



M.S. Fernandes<sup>a,\*</sup>, G.J.V.N. Brites<sup>a</sup>, J.J. Costa<sup>a</sup>, A.R. Gaspar<sup>a</sup>, V.A.F. Costa<sup>b</sup>

<sup>a</sup> ADAI-LAETA, Department of Mechanical Engineering, University of Coimbra, 3030-788 Coimbra, Portugal

<sup>b</sup> Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

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## ABSTRACT

This paper aims to provide the current state of the art of solar adsorption refrigeration systems operating with the single-bed intermittent cycle (also known as basic cycle). A comprehensive literature review has been conducted and it was concluded that this technology, although attractive, has limitations regarding its performance that seem difficult to overcome. Therefore, new approaches were identified to increase the efficiency and sustainability of basic adsorption cycles, like the development of hybrid or thermal energy storage adsorption systems. A survey of the developments in these new research trends is also presented in this paper. It shows that there are simple adsorption cycles which can be attractive alternatives not only to serve the needs for air-conditioning, refrigeration, ice making, thermal energy storage or hybrid heating and cooling purposes, as standalone or integrated systems, but also to meet the demands for energy conservation and environmental protection.

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\* Correspondence to: Departamento de Engenharia Mecânica, Faculdade de Ciências e Tecnologia da Universidade de Coimbra – Pólo II, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal. Tel.: +351 239 790 714; fax: +351 239 790 701.

E-mail address: [marco.fernandes@adai.pt](mailto:marco.fernandes@adai.pt) (M.S. Fernandes).

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## 1. Introduction

For many years, usual vapor compression refrigeration systems typically operated with synthetic refrigerants, such as CFCs, HCFCs or HFCs. When released into the atmosphere, such refrigerants deplete the ozone layer and/or contribute to the greenhouse effect. In the late 1980s, it was estimated that the emissions of these compounds by refrigeration machines, resulting from anomalies during operation or after their useful life, accounted for 33.3% of the greenhouse effect [1]. As a result, several protocols, like the Montreal Protocol (1987) or the Kyoto Protocol (1997), were established in order to phase out, or at least to considerably reduce, the emissions of these refrigerants [2,3]. However, the situation continues claiming for the development of alternative technologies operating with environmentally friendly substances, especially due to the increasing emissions of HFCs, although the emission of CFCs and HCFCs have been decreasing since the late 1980s [4,5].

Furthermore, the ever increasing energy consumption worldwide makes it urgent to find new ways to use the energy resources in a more efficient and rational way. It is estimated that the global energy consumption will increase by 71% between 2003 and 2030 [6]. In addition, currently 80% of the energy on Earth comes from fossil fuel resources [7]. Usual vapor compression refrigeration cycles are electrically powered, consuming large amounts of high quality energy, which significantly increases the fossil energy consumption; and also largely contributing to the greenhouse effect. The International Institute of Refrigeration in Paris estimated that approximately 15% of all the electricity produced worldwide is employed for air-conditioning and refrigeration processes [8]. Moreover, electricity peak demands during summer are becoming more and more frequent due to the general increase in air-conditioning and refrigeration equipment usage.

In another perspective, a considerable percentage of the world population inhabits in remote areas where the electricity supply is scarce, deficient or even non-existent, and so it is estimated to continue over the next decades. The need for refrigeration systems in these locations is of extreme importance since, due to the electricity shortage, conventional refrigeration equipment cannot be used, for instance, in food and medicines storage, ice making or even for air-conditioning.

Therefore, the awareness on issues such as the decrease of fossil fuel resources (with the consequent increasing prices of energy), the severe environmental problems or even the location challenges (e.g., remote areas) require the development of new technologies and led the humankind to look with greater interest for ecological and renewable energy sources. These include wind, solar, hydropower, biomass and geothermal energies, or even thermal waste from various processes. Solar energy is currently a subject of great interest, and refrigeration is a particularly attractive application due to the coincidence between the peak of cooling demand and the solar radiation availability. Thus, systems that have the ability to harness solar energy (or other forms of low-temperature thermal energy), as the adsorption devices, present themselves as interesting alternatives in an intelligent energy management. Recently, adsorption refrigeration processes have been investigated (theoretically and experimentally) and proposed as an alternative to vapor compression refrigeration systems, attempting to preserve the production and efficiency

level of traditional systems, and becoming one of the most promising solar refrigeration methods [3].

When comparing with traditional refrigeration technologies, adsorption cooling systems are not cost-competitive, and have some technical drawbacks, such as low coefficients of performance (COP), low specific cooling powers (SCP), and poor heat and mass transfer on the adsorbent beds, which makes the systems more bulky and expensive [9,10]. Moreover, in the case of solar refrigerators, the energy source is intermittent and can also be highly irregular (e.g., overcast days, seasons). However, these systems promote significant primary energy savings in comparison with common mechanical vapor compression refrigeration systems, and have simpler control, no vibration, no noise, lower operation and maintenance costs, lower environmental impact (operate with non-polluting refrigerants), and are simpler and more robust [10]. Compared with the absorption systems, adsorption systems can be powered over a large range of heat source temperatures, are more robust and less sensitive to physical impacts, do not present corrosion problems due to the working pairs normally used, and are less complex because they contain fewer moving parts [10,11]. The absorption systems, while working in a similar basis (using a heat source to drive the cooling system) and usually being more energy efficient, present the relative drawbacks stated above, mostly due to the operation with liquid sorbents, contrarily to adsorption systems (solid sorbents).

Therefore, the adsorption refrigeration systems appear as a good alternative to replace (or integrate) the traditional refrigeration systems by more environmentally friendly systems, which can be powered by renewable energy sources and contribute to a sustainable development, meeting the current international directives.

Researchers worldwide are working to improve the performance of adsorption cooling systems in order to overcome its current technical and economic issues. Most research works are related to the evaluation of adsorption and physical-chemical properties of the working pairs, development of predictive models of their behavior when working under different conditions, and the study of the different types of cycles [10]. There are several types of adsorptive refrigeration cycles: basic cycle, continuous heat recovery cycle, mass recovery cycle, thermal wave cycle, convective thermal wave cycle, cascade multi-effect cycle, among others [12]. However, the literature review and discussion about the applications and future research trends on the present paper is mainly focused on the basic adsorption cycle, since this is the simpler cycle and the basis for all the adsorption systems.

## 2. The process

### 2.1. Principles of adsorption

The adsorption phenomenon is the result from the interaction between a solid and a fluid (refrigerant) based on a physical or chemical reaction. Physical adsorption occurs when the molecules of refrigerant (adsorbate) fix themselves at the surface of a porous solid element (adsorbent) due to Van der Waals forces, thus leading to the accumulation of a substance on the surface of another. By applying heat, the adsorbate molecules can be released (desorption), whereby this is a reversible process. In turn, the

**Nomenclature**

$A_c$	collector area ( $\text{m}^2$ )
COP	coefficient of performance
$c_p$	specific heat at constant pressure [ $\text{J}/(\text{kg K})$ ]
$G$	solar heat flux density ( $\text{W}/\text{m}^2$ )
$h_{fs}$	latent heat of solidification ( $\text{J}/\text{kg}$ )
$h_{fv}$	latent heat of vaporization ( $\text{J}/\text{kg}$ )
$m$	mass ( $\text{kg}$ )
$P$	pressure ( $\text{Pa}$ )
$Q$	heat ( $\text{J}$ )
$T$	temperature ( $^{\circ}\text{C}$ , $\text{K}$ )
$X$	adsorbate content (mass of adsorbate by unit mass of dry adsorbent) ( $\text{kg}_{\text{adsorbate}}/\text{kg}_{\text{adsorbent}}$ )

**Greek symbols**

$\Delta$	difference; variance
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**Subscripts**

a	adsorption
c	condensation
d	desorption/regeneration
e	evaporation
$\ell$	liquid phase
max	maximum
min	minimum
r	refrigerant
s	solid phase or solar

chemical adsorption results from the ionic or covalent bonds formed between the adsorbate molecules and the solid substance. The bonding forces are much greater than that of physical adsorption, releasing more heat. However, the process cannot be easily reversed. Besides, this type of bonding promotes the chemical alteration of the adsorbed substance, thus the adsorbate and adsorbent molecules never keep their original state after adsorption. Therefore, most of the adsorption refrigeration systems mainly involve physical adsorption [11,13].

When fixed beds of adsorbent are employed, the cycle can operate without any moving parts. This results in a quiet and silent operation, simplicity, high reliability and long lifetime. On the other hand, it leads to intermittent cycle operation, with the adsorbent bed alternating between the adsorption and desorption stages. Thus, when continuous cooling effect is required, two or more adsorbent beds must be operating out of phase, assuming that the heat source is always available, which is not the case of solar radiation [2].

## 2.2. Basic solar adsorption refrigeration cycle

Solar energy is the energy source of most adsorption devices operating with the basic cycle. In the remaining cases the components are kept unchanged, the main difference being the heat collection method.

A solar adsorption refrigerator based on the basic adsorption refrigeration cycle does not require any mechanical or electrical energy, just thermal energy, and it operates intermittently according to the daily cycle. Like a simple vapor compression system, these adsorption systems are closed systems, comprising a compressor, a condenser and an evaporator. However, in this case, the compressor is an adsorber powered by the thermal energy, and the cooling effect is achieved by the evaporation of a refrigerant while the vapor produced is adsorbed by the adsorbent layer in the adsorber. The adsorbed content of refrigerant varies cyclically, depending on the adsorbent temperature and system pressure, which varies between a maximum limit set by the condensation pressure and a minimum limit imposed by the evaporation pressure.

In its simplest form, a solar refrigerator is a closed system consisting of a solar collector containing the adsorbent bed (hermetically sealed and painted in black, to optimize the solar

radiation absorption), a condenser, a receiver equipped with a 2-way valve and a cold box with the evaporator inside (Fig. 1).

The basic adsorption cycle consists of four stages (two isobar and two isosteric lines), which can be represented in the

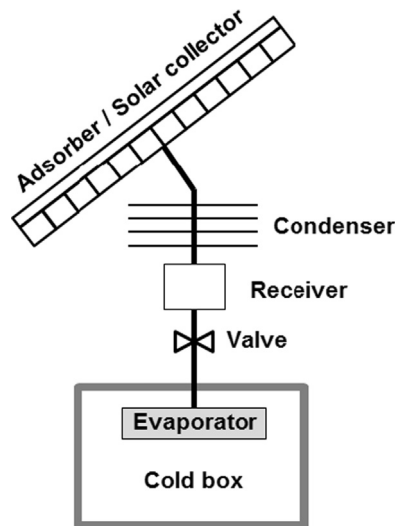


Fig. 1. Main components of a solar adsorption cooling device.

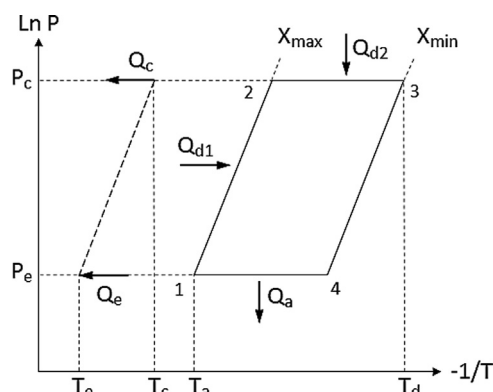


Fig. 2. Basic adsorption cycle (Clapeyron diagram).

Clapeyron diagram (Fig. 2). The process starts at point 1, when the adsorbent is at temperature  $T_a$  (adsorption temperature) and at a low pressure  $P_e$  (evaporation pressure), and the content of adsorbed refrigerant is at its maximum value  $X_{\max}$ . The valve which isolates the condenser from the evaporator is closed and, as heat  $Q_{d1}$  is applied to the adsorbent, both temperature and pressure increase along the isosteric line 1–2 (equivalent to the compression stage in the vapor compression cycle), while the mass of adsorbed refrigerant remains constant at the maximum value. Upon reaching the condensing pressure  $P_c$ , at point 2, the desorption process starts, when the progressive heating ( $Q_{d2}$ ) of the adsorbent from point 2 to 3 (equivalent to the condensation stage in the vapor compression cycle) causes the adsorbent to release the refrigerant vapor, which is liquefied in the condenser (releasing the condensation heat,  $Q_c$ , at the condensation temperature  $T_c$ ) and then collected in a receiver (or flows directly into the evaporator, if there is no receiver nor valve). This stage ends when the adsorbent reaches its maximum regeneration temperature,  $T_d$ , and the adsorbate content decreases to the minimum value  $X_{\min}$  (point 3). Then, the adsorbent cools down along the isosteric line 3–4 (equivalent to the expansion stage in the vapor compression cycle), while the adsorbed refrigerant content remains constant at the minimum value. During this phase, the valve is opened, allowing for the refrigerant to flow into the evaporator, and the system pressure decreases until it reaches the evaporator pressure  $P_e$ , equalizing the refrigerant vaporization pressure (point 4). Afterward, the adsorption–evaporation phase 4–1 occurs (equivalent to the evaporation stage in the vapor compression cycle), producing the cooling effect  $Q_e$  in the evaporator, at evaporation temperature  $T_e$ . At this stage, the vaporized refrigerant in the evaporator flows to the adsorber where it is adsorbed until the maximum content  $X_{\max}$  is reached, at point 1. During this phase, the adsorbent is cooled down until it reaches the adsorption temperature  $T_a$ , by rejecting the sensible heat and the heat of adsorption,  $Q_a$ . At the end of this phase, the valve is closed (to prevent condensation to occur later on in the evaporator) and the cycle restarts [8,14]. In the solar adsorption refrigeration cycle, stages 1 to 3 correspond to the daytime period and the stages 3 to 1 to the nighttime period.

### 2.3. Coefficient of performance

The coefficient of performance (COP) of a refrigeration system is the ratio between its capacity to remove heat from a cold source and the energy supplied for its operation. This ratio is a measure of the conversion of energy supplied to the system into the output cooling capacity, i.e., the efficiency of the cooling system. It is very useful particularly in the comparison between similar systems, operating with the same basic cycle and the same technology.

In the case of a solar refrigerator, the heat removed from the cold source ( $Q_e$ ) corresponds to the cooling effect produced at the evaporator. As for the energy supplied to the system, when considering only the energy that is effectively transferred to the adsorber to promote its regeneration/desorption ( $Q_d = Q_{d1} + Q_{d2}$ , in Fig. 2), the COP of the adsorption cycle can be set as

$$\text{COP}_c = \frac{Q_e}{Q_d} \quad (1)$$

This coefficient of performance refers to a settled period of time, generally considered as an entire day.

However, the most common method to define the COP of a solar refrigerator is to consider all the solar energy received by the solar collector surface ( $Q_s$ ). Thus, the solar COP is defined as

$$\text{COP}_s = \frac{Q_e}{Q_s} \quad (2)$$

The solar energy provided to the system ( $Q_s$ ) corresponds to the product of the solar collector surface area ( $A_c$ ) by the integration of the solar radiation flux on the collector surface ( $\dot{G}$ ) during one day of operation

$$Q_s = A_c \times \int_0^{24 \times 3600} \dot{G} dt \quad (3)$$

The calculation of  $Q_e$  can be performed in two distinct ways: considering the total heat extracted by evaporation from the desorbed and condensed refrigerant mass (gross cooling capacity), or considering the effective heat extracted to produce cold or ice in the evaporator (net cooling capacity). In the first case, the gross cooling capacity corresponds to the difference between the refrigerant latent heat of vaporization and the sensible heat required to cool down the refrigerant from the condensing temperature to the evaporation temperature. The gross solar COP is thus defined by

$$\text{COP}_{s|gross} = \frac{Q_e}{Q_s|gross} = \frac{\Delta m_r [h_{v,r} - c_{p,r}(T_c - T_e)]}{A_c \times \int_0^{24 \times 3600} \dot{G} dt} \quad (4)$$

where  $\Delta m_r$  corresponds to the mass of refrigerant desorbed in one operation cycle,  $h_{v,r}$  is the refrigerant latent heat of vaporization,  $c_{p,r}$  is the specific heat of the liquid refrigerant,  $T_c$  is the condensation temperature and  $T_e$  is the evaporation temperature.

On the other hand, based on the effective or net cooling capacity, the net solar COP is defined as,

$$\text{COP}_{s|net} = \frac{Q_e}{Q_s|net} = \frac{m_\ell c_{p,\ell} \Delta T_\ell + m_s h_{\ell s} + m_s c_{p,s} \Delta T_s}{A_c \times \int_0^{24 \times 3600} \dot{G} dt} \quad (5)$$

assuming that the cooling effect is used to cool down the water and possibly to freeze it, and even to cool the ice produced. In Eq. (5),  $m$  is the mass of water,  $c_p$  its specific heat,  $\Delta T$  its temperature variation and  $h_{\ell s}$  its latent heat of solidification;  $\ell$  and  $s$  represent the liquid and solid phase (ice), respectively [15].

If not otherwise stated, the  $\text{COP}_s$  referred throughout the present paper should be understood as the gross solar COP [Eq. (4)]. In the literature, the solar COP differs from author to author, and several authors do not specify which definition they refer to. In such cases, the solar COP assumed in this paper depends on the context in which it is mentioned by the authors, on previous publications from the same authors, or on what is stated in the literature reviews that mention them. Ultimately, it is assumed that the solar COP corresponds to the gross value.

### 2.4. Selection of the working pair

There are several possible adsorbent–adsorbate working pairs that can be used in adsorption refrigeration systems. The choice should be made carefully, since the performance of the system differs according to the chosen working pair. The proper selection depends on the temperature of the heat source, the desired characteristics of the refrigeration system, the properties of the working pair constituents and the affinity between them (which depend on the chemical, physical and thermodynamic properties of the substances), and even on their cost, availability and environmental impact.

#### 2.4.1. Choice of adsorbate

The adsorbate, or refrigerant, must fulfill the following requirements [8,16]:

- Evaporation temperature below 0 °C (for refrigeration purposes; it can be higher in the case of air-conditioning applications);
- Small molecular size so as to facilitate the adsorption effect;



- High latent heat of vaporization and low specific volume when in the liquid state;
- High thermal conductivity;
- Low viscosity;
- Thermally stable with the adsorbent in the operating temperature range;
- Chemically stable in the operating temperature range;
- Non-toxic, non-corrosive and non-flammable;
- Low saturation pressures (slightly above atmospheric pressure) at normal operating temperature;
- Absence of ecological issues, unlike common refrigerants.

The natural refrigerants used in adsorption refrigeration systems generally have zero environmental impact. The most commonly used refrigerants are ammonia, methanol and water, which have relatively high latent heat values (1368, 1160 and 2258 kJ/kg, respectively) and low specific volumes (of the order of  $10^{-3} \text{ m}^3/\text{kg}$ ). Water and methanol operate at sub-atmospheric saturation pressures at the operating temperatures needed, and any infiltration of ambient air immediately results in system malfunction. In the case of ammonia, small leakages can be tolerated for some time, but its saturation pressure of 13 bar at a condensing temperature of 35 °C is highly demanding. Ammonia is toxic and corrosive, while water and methanol are not, but the latter is flammable. Water is the most thermally stable adsorbate, closely followed by methanol and ammonia, in that order. However, even being the cheapest adsorbate, water cannot be used for cooling purposes below 0 °C [17].

#### 2.4.2. Choice of adsorbent

The most important features for choosing a suitable adsorbent are [12,16]:

- Ability to adsorb a large amount of adsorbate when cooled to ambient temperature, to yield a high cooling effect;
- Desorption of most (ideally all) of the adsorbate when heated by the available heat source;
- Low specific heat;
- Good thermal conductivity, to shorten the cycle time;
- Non deterioration and adsorption capacity losses over time or with usage;
- Non-toxic and non-corrosive;
- Chemically and physically compatible with the chosen refrigerant;
- Low cost and wide availability.

The most suitable adsorbent materials must be porous enough (with specific surface of the order of  $600 \text{ m}^2/\text{g}$  or higher [18]) to allow for adsorption of large refrigerant quantities, but this results in low thermal conductivities, which limits the performance of the refrigeration system. Therefore, there must be a compromise between the high porosity required for rapid vapor diffusion and the high density required for good thermal conductivity [19].

The most commonly used adsorbents are activated carbon, zeolite and silica-gel. Activated carbon offers a good compromise between high adsorption and desorption capacities. In turn, natural zeolites need to be present in large quantities since only a small amount of adsorbate is desorbed during the temperature increase. However, the adsorption isotherms of zeolites have extremely non-linear pressure dependence, which is relevant for solar refrigeration applications. Contrarily, activated carbon and silica-gel present almost linear pressure-dependent isotherms. Silica-gel satisfies most of the criteria listed above, however it is expensive and may not be available in most countries. Besides, the deterioration phenomenon of the adsorption capacity and aging of silica-gel is another current issue [12,17,20].

It should be mentioned that there are several variants of the mentioned adsorbent substances. Basic adsorbents can be doped to present better performances when applied in the adsorption refrigeration systems. For example, Gordeeva et al. [21] presented a study regarding a family of new adsorbent materials to interact with methanol–salts in mesoporous silica, to be used in air-conditioning devices powered by low-temperature heat sources. Furthermore, at the end of the 20th century, an activated carbon fiber was developed to be applied in adsorption cooling devices. An example was described by Vasiliev et al. [22], who reported the development of a solar refrigerator prototype using the activated carbon fiber – ethanol and the activated carbon fiber – methanol working pairs. Wang et al. [23] studied a specially treated activated carbon fiber and concluded that it has two to three times higher capacity for methanol adsorption than standard activated carbon, with the further advantage of shorter adsorption times. Also concerning this subject, Wang et al. [24] and Al-Alili [25] presented several studies regarding the performance enhancement of several adsorbents by combination with other substances.

#### 2.4.3. Working pairs

There are several studies regarding adsorbent–adsorbate working pairs for adsorption refrigeration systems, pointing their characteristics, performances, advantages and disadvantages. The most commonly used working pairs are: zeolite–water, silica-gel–water, activated carbon–methanol and activated carbon–ammonia [8].

Silica-gel–water is ideal for solar energy applications due to its low regeneration temperature, requiring low grade heat sources, commonly below 85 °C. Moreover, water has the advantage of having a greater latent heat than other conventional refrigerants. It is suitable for air-conditioning applications with high chilled water flows, where high evaporation temperatures can be used (it is widely used in adsorption chillers). However, this pair has a low adsorption capacity as well as low vapor pressure, which can hinder mass transfer. Furthermore, this working pair requires vacuum conditions in the system, whereby any non-condensable gas will cause a significant reduction in the system's performance [4,24,26,27].

Activated carbon–methanol is one of the most common working pairs in adsorption refrigeration systems. It also operates at low regeneration temperatures (care must be taken since regeneration temperatures above 120 °C promote the decomposition of methanol), while its adsorption–evaporation temperature lift is limited to 40 °C. This pair is also characterized by its large cyclic adsorption capacity, low adsorption heat, low freezing point and high evaporation latent heat of methanol. However, activated carbon has a low thermal conductivity, acting like a thermal insulator and causing a decrease in the system's COP, and like the silica-gel–water pair, activated carbon–methanol also operates at vacuum conditions. Besides, methanol must be used with caution due to its high toxicity and flammability [14,26,28].

In turn, the activated carbon–ammonia pair requires regeneration temperatures that can exceed 150 °C. Its adsorption heat is similar to that of the pair activated carbon–methanol, but it requires higher operating pressures, which enhances the heat and mass transfer performance and reduces the cycle time, also preventing the infiltration of air into the system. All these factors help to increase the specific cooling capacity of the system. Moreover, this pair suitability to high temperature energy sources and the high cooling capacity of ammonia, make it even more attractive to researchers. However, the activated carbon has a lower adsorption capacity with ammonia than with methanol; furthermore, care must be taken due to the ammonia toxicity,

**Table 1**  
Summary of solar adsorption systems operating with the basic cycle.

Working pair	Reference	Year	Country	Application	Solar collector type	Area (m <sup>2</sup> )	Ice mass produced	Solar COP	Solar radiation	Te (°C)	Type
Activated carbon – Methanol	Delgado et al. [31]	1982	France	Ice maker		4	25 kg/day	0.15 (syst)			Simulation
	Pons and Guillemot [32]	1986	France	Ice maker	Flat plate	6	6 kg/(m <sup>2</sup> .day)	0.10–0.12 (net)	16–19 MJ/day	– 5	Experimental
	Pons and Grenier [109]	1987	France					0.1–0.12 (net)	19–22 MJ/(m <sup>2</sup> .day)		Experimental
	Passos et al. [110]	1989	Brazil					0.156 (net)			Simulation
	Lemmini and Meunier [111]	1990	Morocco	Refrigerator	Flat plate		–	0.114	20 MJ/m <sup>2</sup>		Simulation
	Medini et al. [112]	1991	Tunisia	Ice maker		0.8	4 kg/day	0.067			Experimental
	Boubakri et al. [37,38]	1992	Morocco	Ice maker		1	4 kg/day	0.12 (net)	19.5 MJ/(m <sup>2</sup> .day)		Experimental
	Tan et al. [113]	1992	China	Ice maker		1.1	3 kg/day	0.09	22 MJ/(m <sup>2</sup> .day)		Experimental
	Exell et al. [33]	1993	Thailand	Ice maker	Flat plate w/tubes	0.97	4 kg/day	0.1–0.123 (net)		– 7 to –12	Experimental
	Headley et al. [114]	1994	Trin. Tobago	Ice maker	CPC	2	1 kg	0.02 (net)	26.8 MJ/(m <sup>2</sup> .day)	– 6	Experimental
	Mhiri and El Golli [34]	1996	Tunisia	Ice maker	Flat plate	4	12.2 kg/day	0.14–0.19	5–17 MJ/m <sup>2</sup>	– 5	Experimental
	Sumathy and Li [35]	1999	China	Ice maker	Flat plate	0.92	4–5 kg/day	0.1–0.12	17–19 MJ/(m <sup>2</sup> .day)	– 6	Experimental
	Boubakri et al. [36]	2000	France	Ice maker	Flat plate w/condenser	1	11.5 kg/m <sup>2</sup>	0.19	29 MJ/(m <sup>2</sup> .day)		Simulation
	Wang et al. [90]	2000	China	Hybrid	Evacuated tube	2	10 kg/day	0.14 (syst)	22–24.6 MJ/day (w/lamp)	– 2	Exp./Sim.
	Leite and Daguinet [115]	2000	Brazil	Ice maker	Flat plate w/tubes	1	7–10 kg/(m <sup>2</sup> .day)	0.124–0.155 (net)	20–23 MJ/m <sup>2</sup>	– 2	Simulation
	Wang et al. [91]	2002	China	Hybrid	Evacuated tube	3	9 kg	0.04–0.05 (syst)	61 MJ/day (w/lamp)	– 1.5	Experimental
	Zhang and Wang [93]	2002	China	Hybrid	Rotational flat plate	0.4 (× 2)	–	0.18	21.6 MJ/day	5	Simulation
	Li et al. [92]	2002	China	Hybrid	Flat plate	1	5.5 kg/m <sup>2</sup>	0.115	17.4 MJ/(m <sup>2</sup> .day)		Experimental
	Li et al. [116]	2002	China	Ice maker	Flat plate	1.5	7–10 kg	0.13–0.14	28–30 MJ/day (w/lamp)		Experimental
	Li and Wang [117]	2002	China	Ice maker	Flat plate	1.5	12.43 kg	0.193			Simulation
	Buchter et al. [36]	2003	Burkina Faso	Ice maker	Flat plate	2		0.09–0.13	22–25 MJ/(m <sup>2</sup> .day)		Experimental
	Anyanwu and Ezekwe [118]	2003	Nigeria	Water cooler	Flat plate w/tubes	1.2	–	0.036–0.057		1 to 8.5	Experimental
	Dai et al. [106]	2003	China	Ventilation	Flat plate	5	–	0.12		8	Simulation
	Khattab [119]	2004	Egypt	Ice maker	Glass shell + reflector		6.9–9.4 kg/(m <sup>2</sup> .day)	0.136–0.159 (net)	17–20 MJ/(m <sup>2</sup> .day)		Experimental
	Li et al. [41]	2004	China	Ice maker	Flat plate	0.94	4 kg/(m <sup>2</sup> .day) 5 kg/(m <sup>2</sup> .day)	0.11–0.12 0.12–0.14	16–18 MJ/(m <sup>2</sup> .day) 18–22 MJ/(m <sup>2</sup> .day)		Experimental Experimental
	Lemmini and Errougani [120]	2005	Morocco	Ice maker	Flat plate	0.72		0.05–0.08	12–28 MJ/m <sup>2</sup>	– 11	Experimental
	Luo et al. [121]	2005	China	Ice maker	Flat plate	1.2	3.2–6.5 kg/m <sup>2</sup>	0.083–0.127 (net)	15–23 MJ/m <sup>2</sup>		Experimental
	Boubakri [40]	2006	France	Ice maker	Flat plate	1	5.2 kg/day	0.14	27 MJ/(m <sup>2</sup> .day)	– 10	Simulation
	Martín [122]	2006	Spain		CPC			0.08–0.1			Simulation
	Leite et al. [44]	2007	Brazil	Ice maker	Flat plate w/tubes + reflector	1 (× 2)	6.05 kg/m <sup>2</sup>	0.085 (net)	23.7 MJ/(m <sup>2</sup> .day)	– 4.6	Experimental
	González and Rodríguez [42]	2007	Spain	Ice maker	CPC	0.55	0 kg	0.096	19.5 MJ/(m <sup>2</sup> .day)	– 1.1	Experimental
	Chekirou et al. [123]	2007	Algeria		Flat plate w/tubes			0.184	26 MJ/m <sup>2</sup>	– 5	Simulation
	Vasta et al. [15]	2008	Italy	Ice maker	Flat plate	1.5	2–5 kg/day	0.045–0.11 (net)			Simulation
	Ogueke and Anyanwu [124]	2008	Nigeria	Water cooler	Flat plate w/tubes	1.2	–	0.023 (net)			Simulation
	González et al. [43]	2009	Spain	Ice maker	CPC	0.55	0.06–0.4 kg/m <sup>2</sup> 2.2 kg/m <sup>2</sup>	0.117–0.087			Simulation
	Hassan et al. [46]	2011	Canada		Flat plate w/tubes	1		0.211	900 W/m <sup>2</sup> (max)		Simulation
	Ahmed et al. [45]	2011	Egypt	Ice maker	Flat plate w/tubes + reflector		1.38–3.25 kg/m <sup>2</sup>	0.07–0.11	12.4–25.2 MJ/m <sup>2</sup>		Simulation Experimental
	Suleiman et al. [95]	2012	Nigeria	Hybrid	Flat plate	2	–	0.024		0	Simulation
	Hassan [125]	2013	Saudi Arabia	Ice maker	Flat plate	2	27.82 kg/day	0.618 (cycle)	24.18 MJ/m <sup>2</sup>	– 5	Simulation
	Qasem and El-Shaarawi [126]	2013	Saudi Arabia	Ice maker	Flat plate w/tubes	1	13 kg/day	0.24	24.84 MJ/(m <sup>2</sup> .day)	– 4	Simulation
	Santori et al. [127]	2014	Italy	Ice maker	Flat plate w/tubes	1.2	5 kg/day	0.08 (net)	28.7 MJ/day	– 12.4	Experimental

Activated carbon–Ammonia	Critoph [47]	1994	England	Ice maker	Flat plate w/tubes	1.4	3–4 kg	0.04 (net)	W/lamp	– 1	Experimental
	Critoph et al. [48]	1997	England		Flat plate w/tubes	1.4		0.061–0.071	13.8–19.8 MJ (w/lamp)	0	Experimental
	Niemann et al. [128]	1997	Germany	Ice maker	CPC	140	500 kg/day	0.43 (cycle)	23 MJ/(m <sup>2</sup> .day)	– 10	Experimental
	Oliveira [49]	2004	Brazil	Ice maker			1.2–1.6 kg/day	0.08			Experimental
	Aghbalou et al. [50]	2004	Spain		CPC			0.144		0	Simulation
	Al Mers et al. [51]	2006	Morocco	Refrigerator	Flat plate w/tubes		–	0.105			Simulation
	El Fadar et al. [52]	2009	Morocco	Refrigerator	CPC+heat pipe		–	0.18			Simulation
	Louajari et al. [129]	2011	Morocco	Refrigerator	Flat plate w/tubes		–	0.111			Simulation
	Tchernev [54]	1982	USA	Refrigerator	Flat plate	1	–	0.15	21.6 MJ/m <sup>2</sup>		Experimental
	Dupont et al. [55]	1982	France	Ice maker	Flat plate	0.8	7 kg/m <sup>2</sup>	0.1			Experimental
Zeolite–Water							3.71–8.14 kg/m <sup>2</sup>	0.04–0.14			Experimental
	Grenier et al. [57]	1988	France	Refrigerator	Flat plate	20	7 kg/m <sup>2</sup>	0.10 (net)	17.8–25.3 MJ/m <sup>2</sup>	– 2.5 to 1	Experimental
	Zhang and Wang [105]	2002	China	Hybrid/Comb.	CPC	2	–	0.33		5	Simulation
	Li et al. [58]	2003	China	Refrigerator	Evacuated tube		–	0.25–0.3 (theor)			Simulation
	Ramos et al. [59]	2003	Peru	Refrigerator	Parabolic solar cooker					– 8.7	Experimental
	Omisanya et al. [61]	2012	Nigeria	Water cooler	CPC	1	–	0.8–1.5 (cycle)	14.7 MJ/m <sup>2</sup>	11	Experimental
	Kreussler and Bolz [62]	n.d.	Germany	Water cooler	Evacuated tube + reflector	3	–	0.08	25.9 MJ/m <sup>2</sup> (w/lamp)	0	Experimental
	Sakoda and Suzuki [63]	1986	Japan		Flat plate	0.25		0.2		5	Simulation
	Kluppel and Guegel [64]	1987	Brazil	Refrigerator	Flat plate w/tubes		–	0.055		< 4	Experimental
				Water cooler	Flat plate w/tubes		–	0.077		12	Experimental
Silica-gel–Water	Gurgel et al. [65]	2000	Brazil	Water cooler	Flat plate w/tubes	1	–	0.17	23.8 MJ/(m <sup>2</sup> .day)	5	Simulation
	Mayor and Dind [66]	2002	Switzerland	Ice maker	Flat plate w/tubes	1		0.10–0.15			Simulation
	Hildbrand et al. [68]	2004	Switzerland	Ice maker	Flat plate w/tubes	2	4.7 kg/(m <sup>2</sup> .day)	0.12–0.23	> 20 MJ/(m <sup>2</sup> .day)		Experimental
	Brites [69]	2013	Portugal	Ice maker	Flat plate	1		0.07		0	Experimental
	Li et al. [73]	2004	China	Ice maker	Flat plate	0.94	0 kg	0.029	18.2 MJ		Experimental
	Bansal et al. [71]	1997	India	Refrigerator	Evacuated tube	2.1	–	0.081	26 MJ/m <sup>2</sup>		Experimental
	Erhard et al. [72]	1998	Germany		Flat plate w/tubes			0.05–0.08		– 5	Experimental
	Qi [94]	2005	China	Hybrid	Evacuated tube	4.2	2.8 kg/m <sup>2</sup>	0.069 (net)	20 MJ/(m <sup>2</sup> .day)	– 15	Experimental
	Illoeje et al. [70]	1995	Nigeria	Ice maker	Flat plate w/tubes			0.14			Simulation
	Maggio et al. [74]	2009	Italy	Ice maker	Flat plate w/tubes	1.5	20 kg/m <sup>2</sup>	0.33 (net)			Simulation
Olive waste–Methanol	Abu–Hamdeh et al. [75]	2013	Saudi Arabia	Refrigerator	PTC w/tubes	3.7	–	0.03 (net)	56.2 MJ/m <sup>2</sup> (on site)	4	Simulation

irritating odor (even at low concentrations) and corrosive nature [4,26].

For the zeolite–water pair, the regeneration temperatures can surpass 200 °C, with an adsorption–evaporation temperature lift up to 70 °C or more. This pair remains stable at high temperatures, and the water latent heat is much higher than that of methanol or other traditional refrigerants. However, a system operating with the zeolite–water pair is more fitted for air-conditioning applications due to the solidification temperature of water, which restrains the freezing process. It also has a significant adsorption heat, greater than that of the silica gel–water pair. Furthermore, the low-pressure evaporation of water promotes a slow adsorption stage and the high desorption temperatures increase the sensible heat of the adsorber. Thus, the specific cooling capacity of these systems is not very high. Besides, the low working pressures can hinder the mass transfer [4,14,26].

Anyanwu and Ogueke [29] evaluated the thermodynamic performance of different working pairs when designing a solar adsorption refrigerator. It was concluded that the activated carbon–ammonia pair presents the best results for ice making, deep freezing and food conservation applications. In turn, the zeolite–water pair is better suited for air-conditioning applications. Because the lowest evaporating temperature of water is 0 °C, and due to its high latent heat of vaporization, suitable for producing chilled water, it is a proper choice for air-conditioning purposes. The activated carbon–methanol pair is also suitable for ice production and freezing applications [2].

The adsorption cooling systems may also be classified according to the system pressure. The typical operating pressure ranges for the low and high pressure adsorption refrigeration systems are 0.01–0.35 bar and 3.0–13.5 bar, respectively [12]. Low pressure systems require careful construction, since any amount of air entering the system may lead to its malfunction, affecting the adsorption, evaporation and condensation processes. By contrast, in high pressure systems, small leaks of refrigerant may not have significant impacts on the system operation, and are easier to detect and repair. For systems using methanol as refrigerant, the ice production requires operation below the atmospheric pressure, thus demanding a vacuum environment. This also happens if water is the refrigerant. In turn, the activated carbon–ammonia pair operates at high pressures, well above the atmospheric pressure [30].

### 3. Solar adsorption refrigeration systems operating with the basic cycle

Solar adsorption refrigeration is one of the most promising technologies, mainly due to its simplicity, low environmental impacts and low maintenance requirements. This technology has been the subject of considerable scientific interest in recent decades, and there are currently a large number of publications about it. Most of them literature describe the construction and test of systems, or numerical models and simulation studies. Many prototypes of solar adsorption refrigeration systems working with the basic cycle have already been successfully tested in different regions of the world, operating under considerably different environmental conditions.

Some of these projects are shortly described below, according to the most common working pairs. Table 1 presents a summary of these systems, including additional research works not mentioned in the text. It compares the systems' technology, adsorbent–refrigerant pairs and the COP of the surveyed systems, among other important parameters. The results should not be directly compared to each another, as they were obtained under different

operating conditions; even though they can be used as a reference of what can be expected from such systems.

#### 3.1. Activated carbon–methanol

One of the first records of application of the activated carbon–methanol pair in adsorption refrigeration systems occurred in France, by the early 1980s, when Delgado et al. [31] developed a numerical study concerning a 4 m<sup>2</sup> solar collector system, reaching an ice production of approximately 25 kg per day, with a COP of 0.15. In the same decade, Pons and Guilleminot [32] developed a solar ice-maker prototype comprising four flat plate solar collectors (total area of 6 m<sup>2</sup>) equipped with dampers to increase the night cooling of the adsorbent bed, two air-cooled condensers and an evaporator able to produce between 30 and 35 kg of ice per day, achieving a net solar COP of 0.10–0.12, for clear sky conditions [solar radiation between 16 and 19 MJ/(m<sup>2</sup> day)].

In the early 1990s, an adsorption refrigerator designed and built in Thailand, comprising a 0.97 m<sup>2</sup> solar flat plate collector consisting of an array of copper pipes, a water-cooled condenser and a cold box with a liquid receiver and an evaporator inside [33]. The achieved net solar COP varied between 0.10 and 0.123, and 4 kg of ice were produced per day. The temperature in the evaporator during most nights was below −7 °C, reaching −12 °C sometimes.

Mhiri and El Golli [34] described the study of a solar adsorption refrigerator working with the activated carbon–methanol pair, in order to build an industrial system. The device operated intermittently and had a collecting area of 4 m<sup>2</sup> on the adsorbent container wall. The maximum solar COP ranged from 0.14 to 0.19, for a solar radiation flux between 5 and 17 MJ/m<sup>2</sup>, respectively, and producing 12.2 kg of ice daily at −5 °C.

At the end of the last century, in Hong Kong, a solar refrigerator was designed and built, comprising a household type charcoal inside of a 0.92 m<sup>2</sup> flat plate solar collector [35]. The system was capable of producing 4–5 kg of ice daily, at a temperature of −6 °C in the evaporator, for a daily solar radiation between 17 and 19 MJ/m<sup>2</sup>, and achieving solar COP values of 0.1–0.12. By the same time, a solar

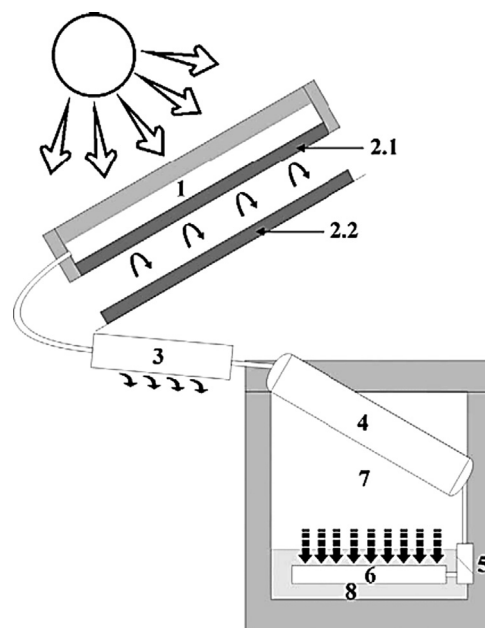


Fig. 3. Solar adsorption refrigerator with ventilation dampers: 1 – solar collector–adsorber, 2.1 – ventilation dampers in closed position, 2.2 – ventilation dampers in open position, 3 – condenser, 4 – graduated bottle, 5 – check valve, 6 – evaporator, 7 – cold cabinet and 8 – ice storage [36].



refrigerator with a 2 m<sup>2</sup> solar collector, equipped with ventilation dampers to increase night cooling of the adsorbent bed (Fig. 3), was tested in Burkina Faso [36]. The solar COP of this machine ranged between 0.09 and 0.13 when the daily solar radiation values were between 22 and 25 MJ/m<sup>2</sup>. The ice produced during the adsorption stage was used to preserve the temperature of the cold box at 5 °C during the day. This device showed better performance compared to similar prototypes, such as a 1 m<sup>2</sup> flat-plate-collector solar refrigerator tested in Morocco, which produced 4 kg of ice per day (daily solar radiation of 19.5 MJ/m<sup>2</sup>), with a net solar COP of 0.12 [37,38].

In 2000, Boubakri et al. [39] presented a numerical model of a solar cooling unit comprising a flat plate solar collector/condenser with a surface area of 1 m<sup>2</sup>, consisting of two identical shells, the upper one operating as a solar collector and the lower one as a condenser. Considering the system's components optimal values and ideal meteorological conditions, the estimated daily ice production was about 11.5 kg/m<sup>2</sup>, with a solar COP of 0.19, for a daily solar radiation of 29 MJ/m<sup>2</sup>. In a subsequent project, the same authors designed a new prototype containing only one heat exchanger which works alternately as a condenser and as an evaporator (Fig. 4) [40]. It is also provided with ventilation dampers for enhancing the night cooling effect of the adsorbent bed, which was one of the limitations of the previous prototype. This configuration considerably reduced the weight of the whole system and therefore the manufacture costs. The system operation was simulated using a mathematical model, predicting a production of 5.2 kg of ice per day (at −10 °C) with a solar COP of 0.14, for a daily solar radiation of 27 MJ/m<sup>2</sup>.

Li et al. [41] described the development of a solar refrigerator operating without any valves or moving parts, manufactured and tested in China. The 0.94 m<sup>2</sup> flat plate collector consists of an insulated box whose surface is coated with a selective coating and with the adsorber placed inside, where several fins increase the heat transfer. The condenser is air-cooled and the evaporator is partially immersed in a water tank located inside the cold box. For a daily solar radiation flux between 16 and 18 MJ/m<sup>2</sup>, the system can produce 4 kg of ice per day and per m<sup>2</sup> of collector, achieving a solar COP between 0.11 and 0.12. Later, the same authors developed a new optimized solar refrigerator producing 5 kg of ice per m<sup>2</sup> of collector and per day (daily solar radiation flux between 18 and 22 MJ/m<sup>2</sup>). The solar COP ranged between 0.12 and 0.14.

González and Rodríguez [42] presented a solar refrigeration system comprising 0.55 m<sup>2</sup> parabolic solar collector with 4 parallel tube receptors containing the bed of activated carbon (Fig. 5). The condenser consists of a cylindrical chamber crossed by cooling water pipes from a water tank attached to the system. The cooling water flow is promoted by an electrically driven pump powered by

a photovoltaic module. The evaporator consists of several vertical pipes, each surrounded by a small cylindrical tank containing the water to refrigerate. Experimental tests led to a maximum solar COP of 0.1, while the evaporator temperature reached −1.1 °C, corresponding to 19.5 MJ/m<sup>2</sup> of daily solar radiation. It was possible to cool down 5 L of water from 23 °C to 2 °C, though not being able to produce ice. Subsequently, the same research group developed a numerical model for simulation and optimization of the system [43]. Through minor improvements of the system and different operation conditions (e.g., a more compact design of the cold box and better sunshine conditions) it was possible to obtain solar COP values between 0.09 and 0.12, corresponding to daily ice productions of 0.4 kg/m<sup>2</sup> and 0.06 kg/m<sup>2</sup>, respectively.

In Brazil, Leite et al. [44] analyzed the performance parameters of an experimental solar adsorption refrigeration device with 2 × 1 m<sup>2</sup> collector area. The solar collector/adsorber is multi-tubular and thermally insulated by a transparent plastic material. These sides can be removed during the night to help cooling the adsorber. Semi-cylindrical reflectors concentrate the solar radiation on the collector side that is not directly irradiated by the Sun. The condenser is immersed in water to facilitate the heat exchange. The layout of the device is presented in Fig. 6. Experimental tests conducted in a region along the Equator were made between October and December, in clear, partly cloudy and over-cast sky conditions, resulting in evaporator temperatures of −4.6, −2.5 and −1.8 °C and daily ice productions of 6.05, 2.10 and 0 kg per m<sup>2</sup> of collector, respectively. Regarding the test conditions for the clear sky day, the net solar COP obtained was 0.09.

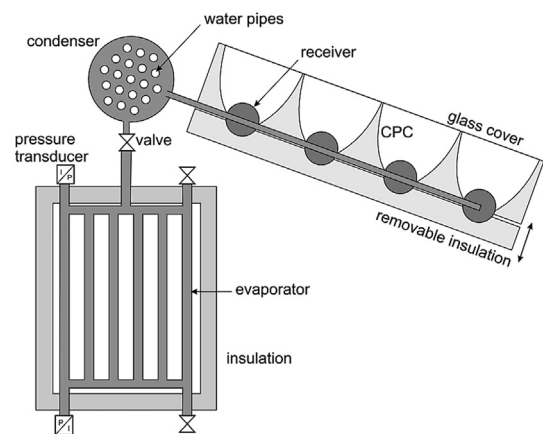


Fig. 5. Solar refrigerator with parabolic collector [42].

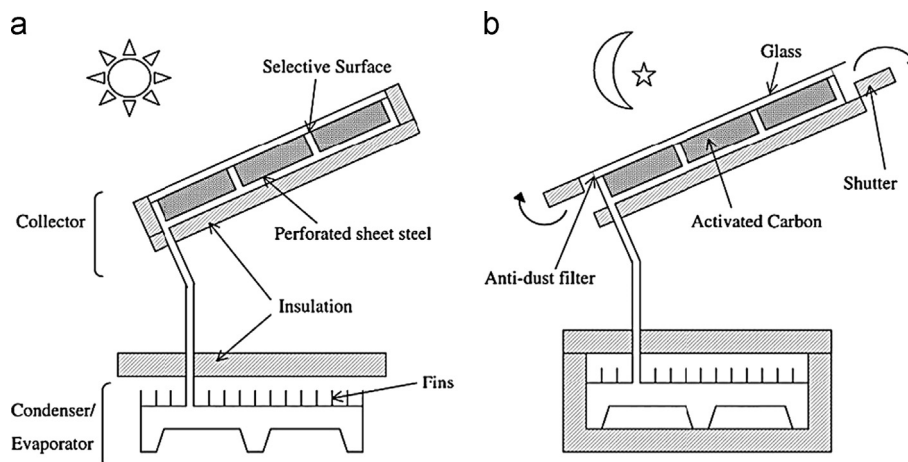


Fig. 4. Solar refrigerator with condenser/evaporator: (a) daytime operation and (b) nighttime operation [40].

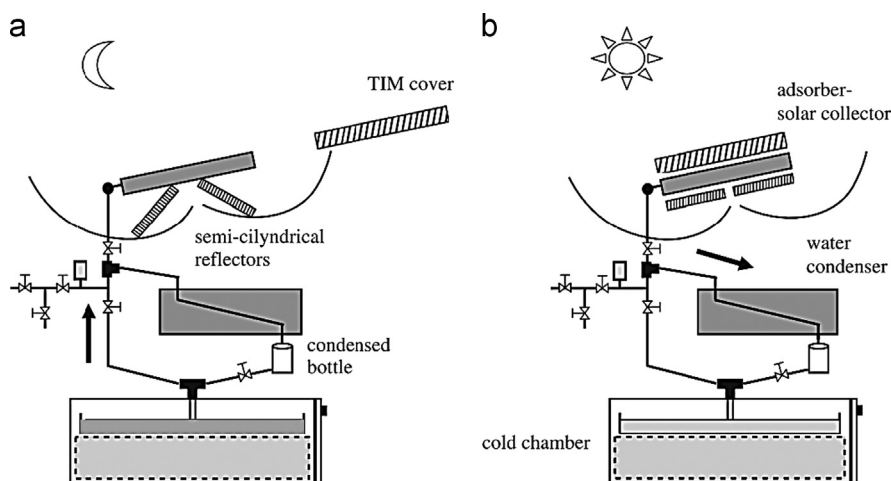


Fig. 6. Solar refrigerator tested in Brazil: (a) refrigeration stage and (b) regeneration stage [44].

In Italy, Vasta et al. [15] presented the numerical model of a solar adsorption refrigerator which simulates the different stages of the thermodynamic cycle and the processes occurring in the system components, which are: a 1.5 m<sup>2</sup> solar collector, containing the adsorbent bed, a condenser and a cold box (having inside an evaporator and the water to freeze). From the results of yearly simulations, it was found that for most of the year (February–October) the system has the ability to produce between 4 and 5 kg of ice per day. For the colder months (November–January), it is possible to produce 2–3.5 kg of ice per day. The average monthly net solar COP ranged from 0.05 (July) to 0.11 (January), with a yearly average COP of 0.07.

More recently, Ahmed et al. [45] described the construction of a solar adsorption refrigerator operating with the activated carbon–methanol pair, with small copper particles added to the adsorbent bed to improve the heat transfer process. A reflector was used to concentrate the solar radiation. This system was tested under the meteorological conditions of Cairo, resulting in the daily ice production of 1.38–3.25 kg per m<sup>2</sup> of collector, with a solar COP ranging between 0.07 and 0.11, while the solar radiation varied between 12.4 and 25.2 MJ/m<sup>2</sup>.

In Canada, Hassan et al. [46] presented a theoretical simulation model of a tubular solar adsorption refrigeration system using the activated carbon–methanol working pair. The 1 m<sup>2</sup> flat plate solar collector consists of several steel pipes containing the adsorbent. From the test results, it was found that the solar COP value was 0.21, while the solar radiation intensity reached a maximum of 900 W/m<sup>2</sup>.

### 3.2. Activated carbon–ammonia

In the late 1980s, Critoph [47] developed a simple low cost solar refrigerator operating at high pressure with the activated carbon–ammonia pair, which was recommended by the United Nations for vaccine storage in poor regions. The pipes of a 1.4 m<sup>2</sup> flat plate solar collector contain the adsorbent material inside. It uses transparent thermal insulation to reduce collector heat losses. The coil shaped condenser is immersed in a water tank. The evaporator is also coil shaped and immersed in water, and its temperature reached  $-1^{\circ}\text{C}$  during the experimental tests, producing 3–4 kg of ice per day, with a net solar COP of 0.04. Some years later, the same research team presented an experimental study of another solar adsorption refrigerator [48]. Three types of collector configurations were studied: single glazed, double glazed and single glazed with transparent thermal insulation. For a solar heat input between 13.8 and 19.8 MJ (simulated with incandescent

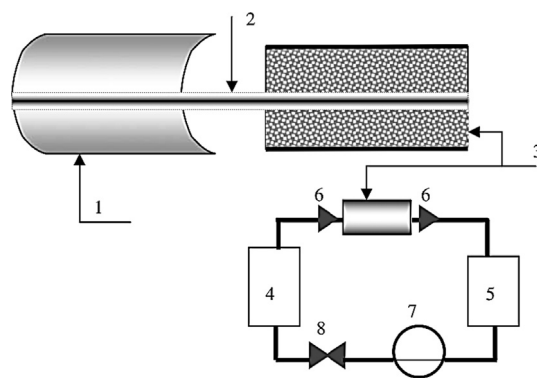


Fig. 7. (a) Simplified scheme of the solar refrigerator: 1 – solar collector, 2 – heat pipe, 3 – adsorber, 4 – evaporator, 5 – condenser, 6 – valves, 7 – tank, 8 – expansion valve and (b) cross section of the receiver assembly: 9 – reflective surface, 10 – glazing, 11 – absorber, 12 – wick [52].

lamps), the solar COP varied between 0.061 and 0.071 (evaporation temperature of  $0^{\circ}\text{C}$ ).

Already in this century, Oliveira [49] designed and tested an adsorption refrigerator comprising tube and shell heat exchangers as reactor, which could be powered, for example, by solar energy. The system produced 1.2 and 1.6 kg of ice per kg of adsorbent daily, when the regeneration temperature was  $75^{\circ}\text{C}$  and  $85^{\circ}\text{C}$ , respectively. The solar COP was 0.08 in both cases. By the same period, Aghbalou et al. [50] developed a numerical model to study an adsorption refrigeration system containing a parabolic solar collector, which transfers the heat to the adsorbent bed through heat pipes (containing water), also promoting the heat dissipation in the adsorption stage. The system reached an evaporation temperature of  $0^{\circ}\text{C}$  with a solar COP of 0.144.

Al Mers et al. [51] presented a numerical model describing the heat and mass transfer processes in a cylindrical finned reactor of a solar adsorption refrigerator. The optimization results showed that the introduction of 6 fins, compared with a bed without fins, increases the solar COP of the system about 45% (from 0.07 to 0.11). Also through numerical modeling, El Fadar et al. [52] simulated, for the summer climate in Morocco, a solar adsorption refrigerator with no moving parts, and with a parabolic solar collector connected to a cylindrical adsorber through a water heat pipe (Fig. 7). The influence of several parameters was analyzed, and it was found that the COP increases as the adsorbent mass is increased, up to a critical value of 14.5 kg, which corresponds to a 72.8 cm collector opening and a solar COP of 0.18.

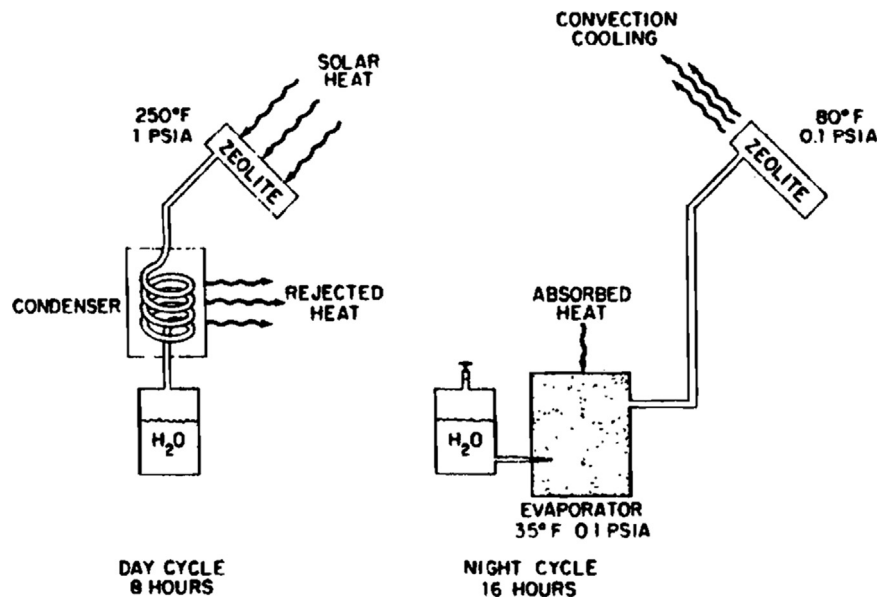


Fig. 8. Tchernev's solar refrigerator [53].

### 3.3. Zeolite–water

The application of this working pair in refrigeration systems emerged in the late 1970s, mainly through the pioneering work of Tchernev, who developed a 100 dm<sup>3</sup> solar refrigerator with a 1 m<sup>2</sup> solar collector (Fig. 8) [53,54]. For a solar energy input of 21.6 MJ, the refrigerator produced 3.24 MJ of cooling per m<sup>2</sup> of collector area, with a solar COP of 0.15. The success of this prototype promoted renewed worldwide interest in solar adsorption cooling. The system was commercialized by Zeopower Co. (USA) [9].

By the same time, in France, Dupont et al. [55] studied a solar refrigerator with a 0.8 m<sup>2</sup> solar collector (shown in Fig. 9, right side), where two operation modes were tested: water-cooled condenser and air-cooled condenser. Experimental tests showed that, in the case of the water-cooled condenser, the solar COP varied from 0.04 to 0.14, producing between 3.71 and 8.14 kg of ice per day, per m<sup>2</sup> of collector. In the case of the air-cooled condenser, the solar COP attained was 0.10, with a daily ice production of 7 kg/m<sup>2</sup>. Also in France, Grenier et al. [57] built a 12 m<sup>3</sup> cold store for food conservation powered by solar energy, with a total solar collection area of 20 m<sup>2</sup> (Fig. 9). The solar COP achieved during clear days [solar radiation between 17.8 and 25.3 MJ/(m<sup>2</sup>.day)] was always around 0.10, corresponding to a daily net cold production of 11 MJ and a daily gross ice production inside the evaporator of about 7 kg per m<sup>2</sup> of collector.

More recently, Li et al. [58] presented the simulation results of a solar refrigerator, in which the zeolite is placed inside the evacuated tubes of the solar collector. The adsorbent can reach 200 °C and the overall system performance is relatively high compared to the previous solar adsorption refrigerators, reaching theoretical solar COP values higher than 0.25.

Also in 2003, Ramos et al. [59] presented experimental results from a solar refrigerator operating with zeolite and water. The system was built by EG Solar [60] and consists of small cartridges containing zeolite, which can be regenerated with any heat source (the EG Solar SK14 parabolic solar cooker by default), a 44 L cold box containing the evaporator, and a manual vacuum pump. There is no need for a condenser because the zeolite is desorbed to the environment. The regenerated cartridge is attached to the cooling box and vacuum must be made. At the end of the cooling phase, the saturated cartridge must be replaced with a regenerated one and vacuum



Fig. 9. Storage room cooled by solar adsorption (on the left) and solar refrigerator device (on the right) (obtained from [56]).

produced again. From the results of tests conducted in Peru, it was found that it was possible to maintain the evaporator temperature below 0 °C for 24 h (reaching −8.7 °C). However, the system had several shortcomings: the SK14 solar cooker was not able to completely regenerate the zeolite cartridges (an electric furnace had to be used); the geometry of the adsorber vessel did not facilitate homogeneity in the adsorption and desorption processes; water froze in the hose connecting the evaporator to the adsorber, obstructing the adsorption process; and it was necessary to open the system in each cycle, introduce distilled water and pump each time in order to get and maintain the necessary low pressure.

In 2012, Omisanya et al. [61] presented a solar adsorption cooling system developed in Nigeria comprising two compound parabolic-concentrator (CPC) solar collectors (1 m<sup>2</sup> of total area), a condenser and an evaporator inside a cold box. The experimental tests resulted in an average temperature of 11 °C in the evaporator throughout the daytime period and a maximum temperature of 110 °C in the adsorber. The average daily-hourly mean cycle COP ranged between 0.8 and 1.5, with an average daily solar radiation of 14.7 MJ/m<sup>2</sup>.



Kreussler and Bolz [62] constructed an experimental device to study the cooling effect obtained with the zeolite–water pair. The zeolite was located inside the evacuated tubes of a 3 m<sup>2</sup> solar collector, which could be heated by means of an artificial lighting source (25.9 MJ/m<sup>2</sup>) and parabolic reflectors. From the experimental results, it was found that a heating temperature of 170 °C yields a solar COP of 0.08, when the water is cooled down to 0 °C inside the cold box.

### 3.4. Silica-gel–water

In 1986, a refrigeration system with a 0.25 m<sup>2</sup> flat plate solar collector containing silica-gel was developed in Japan [63]. To improve the collector heat transfer, it was divided into several blocks with square fins, leading the temperature of the adsorption bed to a maximum of 80 °C. A solar COP of 0.2 was attained. Also in the same decade, Klüppel and Gurgel [64] built and tested in Brazil two adsorption cooling prototypes powered by solar thermal energy: a small domestic refrigerator and a portable water cooler. A solar COP of 0.055 was obtained for the domestic refrigerator with evaporator temperatures below 4 °C, while a solar COP of 0.077 was reached for the portable water cooler with evaporator temperatures around 12 °C.

Gurgel et al. [65] presented the numerical modeling of a solar adsorption water cooling system. The device comprises a 1 m<sup>2</sup> flat plate solar collector with parallel tubes containing the silica-gel inside. The collector can be opened to promote the adsorber cooling during the night, and the removable thermal insulation module can be placed over the collector glass to work as shading element after the desorption stage, when solar energy is no longer necessary. A daily solar radiation of 23.8 MJ/m<sup>2</sup> was considered for the calculations, and it was found that the system has the ability to cool 30 kg of water from 30 °C to 5 °C daily, with a solar COP of 0.17.

At the beginning of the current century, in Switzerland, Mayor and Dind [66] built a portable solar adsorption refrigerator prototype (Fig. 10). The collector has a surface area of 1 m<sup>2</sup>, containing the silica-gel inside its tubes. The cold box is thermally insulated by vacuum panels, and the system contains a special valve that replaces the manual valves from the previous prototypes. This refrigerator system has the capacity to cool down 30 K a mass of 2.5 to 3.7 kg of water in a desert climate. The system stores cold in the form of ice, which allows for 3 days of autonomy in the absence of Sun (8 °C inside the cold box). The authors estimate the solar COP of the system to vary between 0.10 and 0.15 for a hot desert climate, characterized by high temperatures, even during the night. Nevertheless, the numerous system elements did not allow for a simple construction (e.g., high number of welds) and did not ensure a perfect sealing over time. As a result, a new

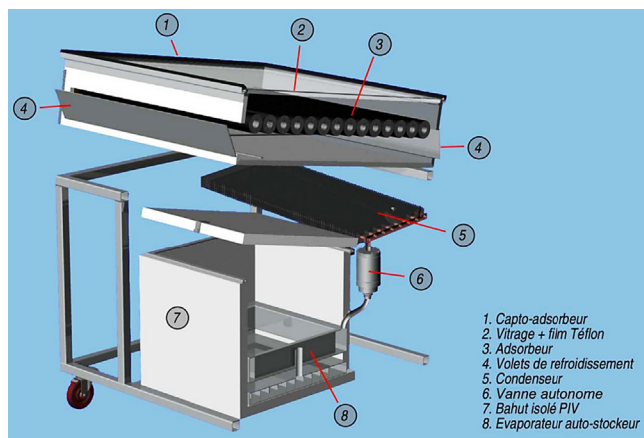


Fig. 10. Solar refrigerator with the silica-gel–water pair [66].

collector was developed, consisting of 30 longitudinal elements (per m<sup>2</sup> of collector), now operating with the zeolite–water pair [67]. This new configuration, with the new working pair, resulted in nearly identical performance values as to the previous version, though reducing the construction problems.

Also in Switzerland, Hildbrand et al. [68] reported the experimental test results with a solar adsorption refrigerator (Fig. 11). The device comprises a 2 m<sup>2</sup> flat plate solar collector with double glazing, and the adsorbent is placed inside its parallel steel tubes. The experimental tests occurred with a 4.1 MJ/day load inside the cold box. The evaporator temperature remained constant over a period of 30 days, during which the solar radiation received by the system was 15.4 MJ/(m<sup>2</sup>.day). The authors estimated a monthly mean solar COP value of 0.16 and a daily ice production of 4.7 kg per m<sup>2</sup> of solar collector.

Recently, a solar adsorption refrigeration system operating with the silica-gel–water pair was developed in Portugal [69]. The system consists of a 1 m<sup>2</sup> flat plate solar collector, a condenser, a condensate receiver and an evaporator inside a cold box (Fig. 12). From the experimental results, it was found that the unit is capable of reaching a solar COP of 0.07, cooling a daily load of 6 kg of water, and still produce a significant amount of ice inside the evaporator to maintain its temperature constant all the time (near 0 °C).

### 3.5. Other working pairs

In addition to the most common working pairs, other pairs have also been investigated. In Nigeria, Ilaje et al. [70] simulated the operation of a solar adsorption refrigerator using the calcium chloride–ammonia working pair. The granular adsorbent is packed in the collector tubes of a double glazed flat plate solar collector. The condenser tubes are cooled by stagnant water whose temperature is maintained below atmospheric temperature by evaporative cooling of the porous sandcrete walls. The evaporator coil is immersed in a water pool inside an insulated box. The solar COP of the system reached 0.14.

Bansal et al. [71] developed a solar refrigerator operating with strontium chloride as adsorbent and ammonia as refrigerant. The system, manufactured by the German company Dornier, comprises a 2.1 m<sup>2</sup> evacuated tube solar collector and has the capacity to produce a daily 4.4 MJ cooling effect. Although a solar COP of 0.14 was predicted, the maximum solar COP obtained was 0.08, when the daily solar radiation was 26 MJ/m<sup>2</sup>. Erhard et al. [72] also used

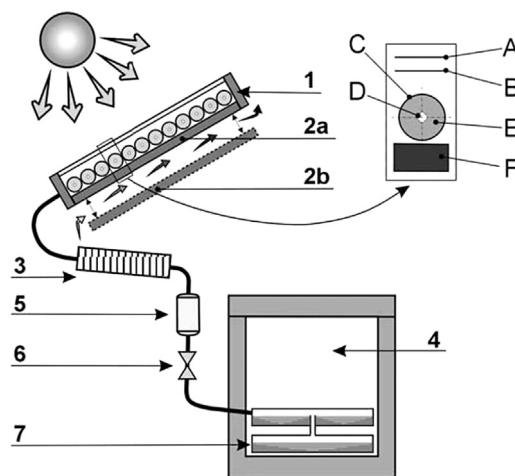


Fig. 11. Solar refrigerator developed by Hildbrand et al. [68]: 1 – with detail: A – glass cover, B – Teflon film, C – tube covered with selective surface, D – central tube for vapour transport, E – silica-gel bed, F – thermal insulation; 2 – ventilation dampers (a – closed, b – open) and 3 – condenser, 4 – cold box, 5 – graduated tank, 6 – valve, 7 – evaporator and ice storage.

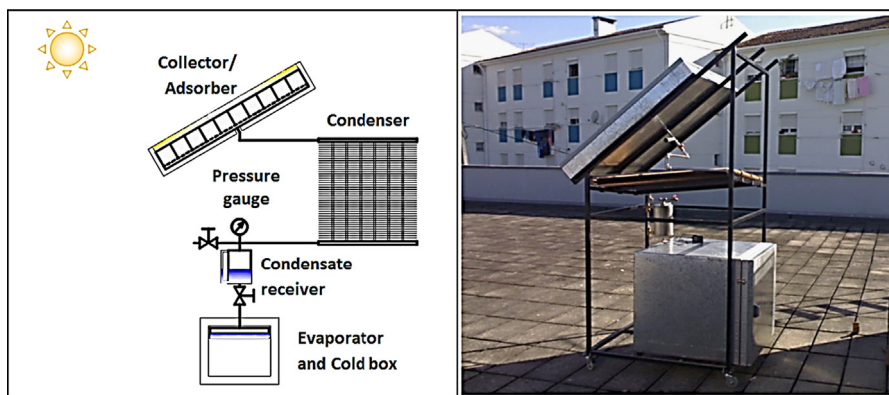


Fig. 12. Solar refrigerator built in Portugal schematic and photo [69].

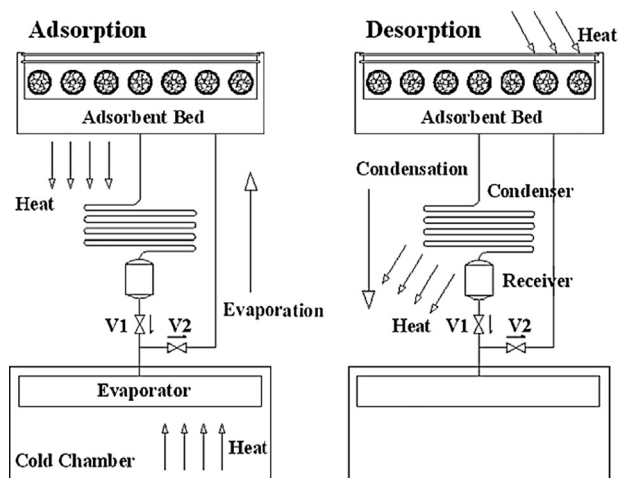


Fig. 13. Solar refrigerator operating with the lithium chloride - silica-gel - methanol working pair [74].

the strontium chloride-ammonia pair in a demonstration adsorption refrigeration device constructed in Germany. However, a global COP of only 0.08 was reached, the evaporator temperature reaching  $-5^{\circ}\text{C}$  during the cycle.

Already in this century, Li et al. [73] tested two working pairs in a solar adsorption refrigerator to determine the system performances under identical conditions – activated carbon-methanol and activated carbon-ethanol. Experimental results showed that, with a solar radiation of  $15.2\text{ MJ}$  and starting from an initial temperature of  $25^{\circ}\text{C}$  in the cold box, the methanol system produced  $2.55\text{ kg}$  of ice, with a solar COP of 0.113, while the ethanol system was not able to produce ice (solar COP of 0.034). In a second test, with a solar radiation of  $18.2\text{ MJ}$  and starting from an initial temperature of  $16\text{--}17^{\circ}\text{C}$  in the cold box, the methanol system produced  $2.6\text{ kg}$  of ice, with a solar COP of 0.105, while the ethanol system produced no ice once again (solar COP of 0.029).

Maggio et al. [74] presented a mathematical model to evaluate the performance of a solar adsorption refrigerator working with methanol as refrigerant and a high adsorption capacity composite material as adsorbent – lithium chloride in the pores of silica-gel. The system consists of a  $1.5\text{ m}^2$  flat plate solar collector, a condenser and an evaporator inside a cold box (Fig. 13). The maximum observed net solar COP was 0.33, with a maximum daily production of  $20\text{ kg}$  of ice per  $\text{m}^2$  of collector.

More recently, Abu-Hamdeh et al. [75] developed a model of a solar adsorption refrigeration system operating with the olive waste – methanol pair. The system comprises a  $3.7\text{ m}^2$  parabolic trough solar collector, a heat storage tank, an adsorber, a

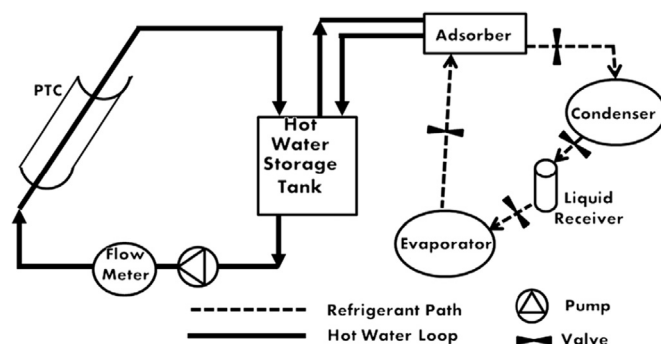


Fig. 14. Schematic diagram of the adsorption refrigeration system operating with olive waste and methanol [75].

condenser, an evaporator, a throttling valve and a circulating pump (Fig. 14). From the simulated results, the lowest temperature attained in the refrigerated space was  $4^{\circ}\text{C}$ , with a net solar COP of 0.03, for a global solar radiation on site of  $56.2\text{ MJ/m}^2$ .

### 3.6. Commercial solar adsorption refrigerators

According to Iloeje and Enibe [76], the first attempts to commercialize adsorption refrigerators were made in the 1920s, using the silica-gel-sulfur dioxide pair, and in the 1950s, with the activated carbon-methanol pair, using only fossil fuels as the heat source. However, these adsorption refrigerators were commercially unsuccessful mostly due to the emergence of more efficient CFC based vapor compression refrigerators using cheap conventional energy, and the interest on solar adsorption refrigeration rapidly declined. It was only after the energy crisis of the 1970s, and especially after the Montreal protocol in 1987 and the Earth Summit of 1992, that the adsorption refrigeration gained a new impetus with the proposal of innovative systems working with solar energy. The early works of Tchernev [53] and Meunier [78] in the late 1970s were crucial for this renewed interest, which grew rapidly in the 1980s.

Some solar adsorption refrigerators have been since put commercially available on the market. In 1988, the French company Brissoneau et Lotz-Marine (BLM) began to market a series of solar adsorption refrigerators operating with the activated carbon-methanol pair (Fig. 15) and also with the zeolite-water pair [37,79]. The Zeopower company (USA) in the early 1980s [54], Solaref (France) [80] and EG Solar (Germany) in the early 2000s [60] also produced and commercialized intermittent solar adsorption refrigerators using the zeolite-water pair.

All the above designs proved to be technically successful but too expensive to penetrate the market [81]. For instance, the unit





Fig. 15. BLM solar ice makers tested in Morocco (obtained from [77]).

price of about US \$1500 for the BLM system for a daily ice production of 5.5 kg was considered too high by about 30% to get a real market [79]. The Zeopower refrigerator was mostly sold for demonstration purposes, costing around US \$1700 per unit [82], while the price for the EG Solar refrigerator was around €900 [60]. The Solaref refrigerator, based on the design developed by Dind et al. [67], was intended to be mainly commercialized in Africa, costing between €2600 and €3700 [80]. Therefore, several companies which produced and marketed solar powered refrigerators have been forced to stop production because of purely economic reasons. An example is Kaptan Aps from Denmark, which produced an intermittent adsorption refrigerator based on the calcium chloride–ammonia pair. The system was technically successful but expensive, and was therefore discontinued. For the same reason, BLM in France, which produced a range of refrigerators using active carbon and methanol, also ceased production [8,83].

More recently, the German company Zeo-Tech GmbH patented a solar-thermal ice maker based on the adsorption principle, operating with the zeolite–water pair [84]. They also developed and patented several other applications based on the adsorption cycle, mostly for and with their industrial customers, like mobile cold containers and a self-cooling beer keg, among others [85].

Despite all efforts to introduce a solar refrigerator or ice maker based in the adsorption principle in the market, the solar photovoltaic refrigerators are still leading. There are currently many companies successfully manufacturing and selling PV-powered vapor compression refrigerators worldwide. For solar adsorption systems, considerable reduction in unit cost or significant improvements in its performances at present costs are still required in order to increase their competitiveness and commercialization potential.

### 3.7. Technology analysis

One can conclude that, although many and disperse efforts have been spent in this subject research and several innovative works have appeared over the last decades, there was no significant improvement of the performance of the solar adsorption refrigeration systems. The solar COP, even for the most recent prototypes, remains relatively low, ranging typically from 10% to 20%. The few higher performances result mainly from simulation works, without a practical validation. This suggests that there are factors limiting the performance of the experimental prototypes which are neglected or underestimated in the works based only on numerical simulation models. The identification of these factors may contribute to improve the performance of the experimental models, especially in the cases where corrective actions can be made. Some possible factors are the surface thermal resistance between the adsorbent bed and the adsorber, the evaporation pressure which may be considered (in the simulation model) equal

to the vapor pressure of the refrigerant but can actually be much lower, or even the tridimensional effects (linear bridges) in heat transfer in the solar collector, especially for small collectors.

There are still limitations that do not allow these systems to compete yet with the common vapor compression refrigeration systems. These include the high initial investment, poor heat management, difficult heat transfer in the adsorbers, and the intermittent (with daily period) and varying character of the operating conditions make the problems of thermal regulation inside the cold compartment, energy storage and automatic operation difficult to solve [2,86]. Nevertheless, due to its autonomy, simplicity and environmentally friendly characteristics, especially the non-dependency on conventional energy sources, solar adsorption refrigeration systems are an attractive alternative to replace or integrate conventional refrigeration systems. Furthermore, if the costs of fossil fuels, transportation, energy conversion, electricity distribution and system maintenance are taken into account, the energy cost associated with the solar adsorption refrigeration systems would be much lower than that of conventional refrigeration systems, and this point is often overlooked [8].

In order to become competitive, the performance of these adsorption systems needs to be increased. However, looking back to the progresses made over the past decades, it seems that the basic solar adsorption refrigeration cycle performance cannot be significantly improved. The majority of the current research works is related with the necessity to improve the adsorber–collector operating parameters and to develop new or enhanced working pairs. On the other hand, several projects and research works have been undertaken to overcome these limitations by developing continuously operation systems with higher performances, recurring to multiple adsorbent beds, mass or heat recovery systems, or multi-stage systems (e.g., adsorption chillers). However, such systems usually require a continuous heat source to operate uninterruptedly, and they are also more complex and expensive. Nevertheless, there are other ways to take advantage of the basic adsorption cycle, maintaining its principle and simplicity.

## 4. Application trends of the basic adsorption cycle

One of the possible solutions for the basic cycle application is to harness the adsorption and/or the condensation heat of the adsorption cycle, which may support the domestic hot water (DHW) needs, or use the adsorption system as a thermal energy storage system. It should be mentioned that water and space heating account for a large part of the residential energy needs (82% in Europe) [87]. Therefore, the addition of new energy technologies, such as adsorption, can greatly assist in reducing the energy costs. Another alternative is the combination of the basic adsorption cycle with other refrigeration cycles, creating hybrid systems, and taking advantage of the different operation stages in each cycle, as well as the best characteristics of each one, resulting in a better overall performance [88].

### 4.1. Heating and cooling hybrid systems

There are already several hybrid systems using the basic adsorption cycle for heat and cold production. Some of these systems are presented below, and summarized in Table 1.

The first hybrid adsorption cooling and heating system was developed by Tchernev in the late 1970s [54]. The system operates with the zeolite–water pair and is shown in Fig. 16. Here, the condenser and the evaporator are combined in a single unit crossed by an external water loop. During the day, the condensation heat is rejected to the external water loop and can be used for providing DHW and space heating during the winter (heat can be

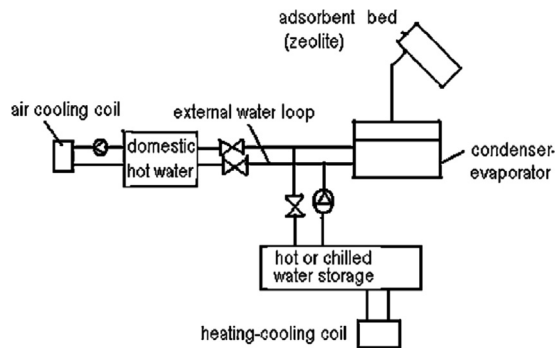


Fig. 16. Zeolite – water system for heating and cooling [53].

stored during the day and used during the night). During the night, the previously condensed water evaporates and is adsorbed by the zeolite, promoting the cooling effect on the condenser/evaporator. This will cool down the water in the external loop, which can be used for air-conditioning or stored for later use. The author stated that it would require about 1 t of zeolite, distributed over 200 ft<sup>2</sup>, to produce 1 t of air conditioning.

Schwarz et al. [89] presented a hybrid heating and cooling system developed by Zeo-Tech. The system operates with the zeolite–water pair, and both the sensible and adsorption heat of the adsorber bed are used for water heating purposes, while the cooling effect, produced during the adsorption–evaporation stage, maintains a cold box at low temperature.

At the end of the last century, Wang et al. [90] developed in China an innovative solar hybrid system for water heating and ice production using the activated carbon–methanol pair (Fig. 17). The adsorber bed is immersed in a water tank and is directly heated by a 2 m<sup>2</sup> evacuated tube solar collector. During the night, the hot water drained from the tank can be used for domestic purposes, while cold water is refilled to the tank, which reduces the adsorber temperature, promoting the adsorption of refrigerant from the evaporator and starting the ice production. During the adsorption stage, the sensible and adsorption heat from the adsorber are transferred to the water in the tank, raising its temperature and producing useful heat. Based on experimental results (electric heating on a 3 m<sup>2</sup> solar collector and more than 100 kg of hot water production), the authors estimated the following results: regarding a 2 m<sup>2</sup> solar collector and 60 kg of hot water production: in the winter case, with a daily solar radiation of 24.6 MJ per day, the system produces 60 kg of hot water at 98 °C and 10.5 kg of ice at –2.5 °C, with an overall system COP of 0.143 (cycle COP of 0.386) and a heating efficiency of 0.795; in the spring case, with a daily solar radiation of 22 MJ, per day the system produces 60 kg of hot water at 91.3 °C and 10 kg of ice at –1.8 °C, with an overall system COP of 0.144 (cycle COP of 0.431) and a heating efficiency of 0.797.

Later, Wang et al. [91] developed a system similar to the previous one, but including a second tank, which serves as hot water reservoir. The system was tested using an electric heating source (1500 W into the 3 m<sup>2</sup> evacuated tube collector). For a 61 MJ supply, the temperature of 120 kg of water in the tank raised from 22 °C up to 92 °C, producing 9 kg of ice at –1.5 °C in the evaporator. The overall system COP reached 0.059 (cycle COP of 0.41). The same research group also developed a new solar hybrid system for heating and cooling with a 1 m<sup>2</sup> flat plate solar collector (Fig. 18), operating with activated carbon and methanol [92]. The main difference to the previous prototypes is the inclusion of the adsorbent bed within the solar collector, so as to recover the sensible and the adsorption heat from the adsorbent bed to produce hot water. It also increased the heat and mass transfer processes in the adsorption and desorption stages. The solar COP

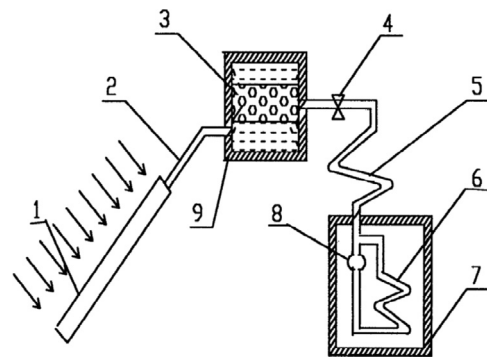


Fig. 17. Solar hybrid system using the activated carbon – methanol pair: 1 – solar collector, 2 – water pipe, 3 – adsorber, 4 – valve, 5 – condenser, 6 – evaporator, 7 – refrigerator (with cold storage), 8 – receiver and 9 – hot water container [90].

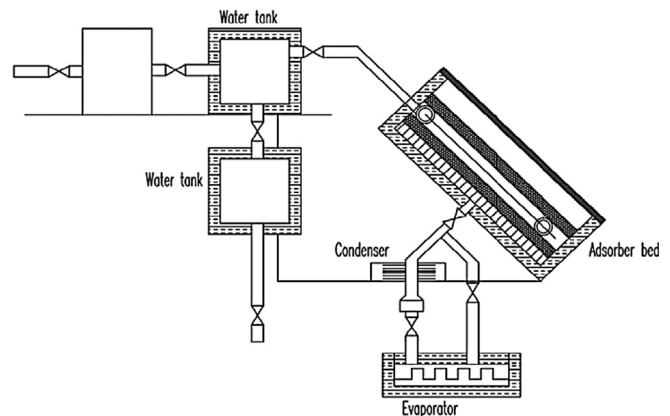


Fig. 18. Heating and cooling hybrid system with the adsorber inside the flat plate collector, using the activated carbon – methanol pair [92].

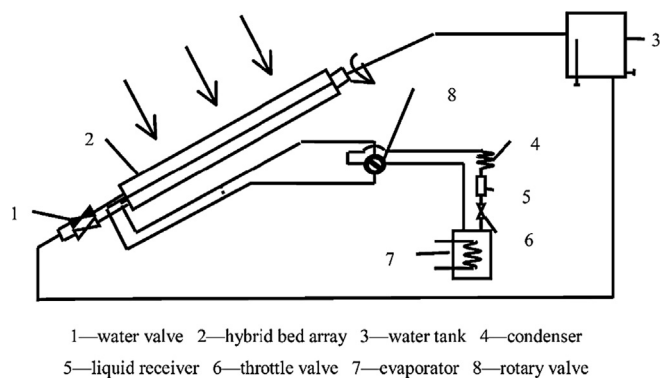


Fig. 19. Continuous solar adsorption cooling and heating system [93].

reached 0.12, yielding daily 5.5 kg of ice per m<sup>2</sup> of collector and 60 kg of hot water (45–50 °C), when the daily solar radiation was about 17.4 MJ/m<sup>2</sup>. The maximum temperature reached in the bed was 110 °C and the heating efficiency was 0.45.

Zhang and Wang [93] designed a continuous-operation hybrid solar adsorption system for heating and cooling purposes, working with the activated carbon–methanol pair (Fig. 19). The results were obtained by simulation. For a daily solar radiation of 21.6 MJ, the system is capable of heating 30 kg of water up to 47.8 °C with an average heating COP of 0.34, while the evaporation temperature reaches 5 °C with a solar COP of 0.18. The upper bed can reach 80–90 °C, after which the collector is rotated by 180° and the upper bed is replaced by the lower bed, which is now heated by solar

energy, while the initially upper bed (now the lower bed) is cooled by cold water coming from a water tank, which flows by natural convection. Each surface (upper and lower) has a heat-collection area of  $0.4 \text{ m}^2$ .

Also in China, Qi [94] built and tested a hybrid solar adsorption prototype for water heating and ice production, operating with strontium chloride and ammonia and a  $4.2 \text{ m}^2$  evacuated tube solar collector. It also comprises a hot water tank, an adsorber, a circulation pump, an evaporator inside a cold box and a condensate receiver. The main difference to other solar hybrid systems is the placement of the adsorber outside the hot water tank (or the collector), thus not depending on hot water consumption to cool down the adsorber during the night. In the experimental tests, for a solar radiation of  $20 \text{ MJ}/(\text{m}^2 \cdot \text{day})$ ,  $180 \text{ kg}$  of water were heated to  $93^\circ\text{C}$  and a temperature of  $-15^\circ\text{C}$  was reached in the evaporator, producing  $11.6 \text{ kg}$  of ice per day. The system net solar COP (based on the amount of ice removed) was  $0.069$ , and the efficiency of the entire system was  $0.67$  ( $0.72$  without ice production). The refrigeration effect produced after one day of operation can be used to keep a  $200 \text{ l}$  cold box below  $5^\circ\text{C}$  for more than  $24 \text{ h}$ .

More recently, in Nigeria, the numerical model of a solar hybrid system for cooling and heating was presented by Suleiman et al. [95]. The system comprises a  $2 \text{ m}^2$  flat plate solar collector and operates with activated carbon and methanol. The simulation results, for a typical year in Kano, Nigeria, considering an evaporator temperature of  $0^\circ\text{C}$  and  $25^\circ\text{C}$  in the condenser, showed an average cooling capacity of  $4815 \text{ kJ}$  (average desorption temperature of  $86^\circ\text{C}$ ), with a solar COP of  $0.02$  (cycle COP of  $0.61$ ) and a heating efficiency of  $0.46$ .

#### 4.2. Thermal energy storage systems

The main goal of the energy storage systems is to accommodate the lag between the energy availability and its necessity. In Europe, it has been estimated that around  $1.4$  million GWh per year could be saved and  $400$  million tonnes of  $\text{CO}_2$  emissions avoided in the building and industrial sectors by more extensive use of heat and cold storage [96]. Moreover, it is estimated that in the near future energy supply will be more unstable than in present, thus being essential to develop efficient and inexpensive energy storage devices [97]. However, innovative storage technologies still face several barriers to their global implementation, especially due to its economic competitiveness compared to fossil fuel technologies, and its long term reliability.

The most usual thermal energy storage methods are the sensible (e.g., water tanks) and latent (ice or phase change materials) heat storage. However, the sorption phenomenon can also be applied for this purpose. In that case, a heat source promotes the dissociation (endothermic process) of a working pair, whose substances can be stored separately. When they come into contact again, heat release occurs (exothermic process). Therefore, the energy can then be stored virtually without any loss, as the heat is not stored in a sensible or latent form, but as a potential, as long as the substances are kept separate.

Sorption storage systems are characterized by high energy densities (higher than sensible or latent heat storage), negligible heat losses and possible long storage periods. Therefore, adsorption thermal energy storage is a promising technology that can provide an excellent solution for long-term thermal energy storage in a more compact and efficient way. Solar thermal energy, thermal surplus energy or waste heat from several processes (e.g., industrial waste heat) can be used to regenerate the adsorbent and promote the energy storage. Thus, it can integrate or even replace the heating and cooling production from fossil fuel systems, reducing the carbon dioxide emissions and lowering the energy demand peaks and the energy production levels [97,98].

The adsorption cycle has already been used in several research projects to promote the thermal energy storage. In 1990, Kaubek and Maier-Laxhuber [99] patented an adsorption apparatus to be used as an electro-heating storage, operating with the zeolite–water pair, alleging  $30\%$  savings in energy consumption. The system can be used as an air heating device or combined with a hot water tank. In the former case (Fig. 20), the adsorbent bed is heated by electric heating rods during the desorption phase, regenerating the adsorbent and releasing the condensation heat into the space to be heated. In the latter case (Fig. 21), during the desorption phase, the condensation heat is released into a water tank, while in the adsorption stage the adsorption heat is transferred to the water tank through a specific closed circuit.

Within the framework of the EU-project MODESTORE, a prototype storage module was developed using silica-gel and water [100]. A spiral heat exchanger containing approximately  $200 \text{ kg}$  of silica-gel is connected to an evaporator/condenser at the bottom of the vessel (Fig. 22). The main advantage of this prototype is its compactness. However, it was found that, with the current working pair, the temperature lift could desorb only  $2\text{--}12\%$  of the water contained in the silica-gel. These values are significantly lower than the silica-gel sorption potential (close to  $35\%$ ) and even lower than the storage density of the water between  $25$  and  $85^\circ\text{C}$ . Further disadvantages when comparing with conventional energy storage systems are: the need for additional components (e.g., heat exchangers, tanks, hydraulic connections), sensible heat losses in the adsorbent bed, and the need of a heat source to promote the evaporation effect. Thus, the authors concluded that this system was not suitable for short-term thermal energy storage, being effective just on the long term.

Regarding the previous system, Wagner et al. [101] reported that, for application in a family house, a suitable low temperature heat sink must be present. Possible solutions are the bottom section of a DHW tank, solar collectors during the night or a low temperature heating system. In addition, several modifications to the system would be required: separation of the evaporator and the condenser by a valve, constant turbulent flow in the evaporator/condenser, and improvement of the heat transfer in the heat exchangers.

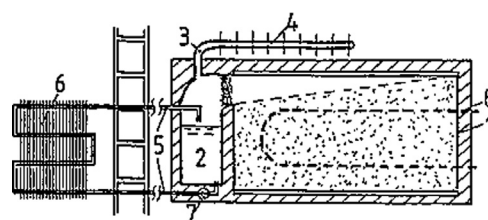


Fig. 20. Air heating electro-heating storage device: 1 – adsorbent, 2 – condensate receiver, 3, 5 – connection pipes, 4 – condenser, 6 – heat collector, 7 – pump and 8 – electric heating rods [99].

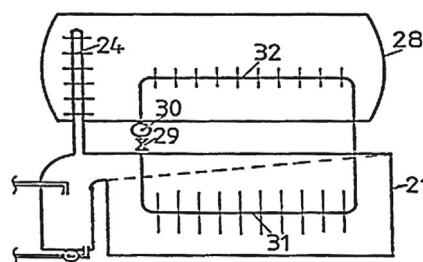


Fig. 21. Water heating electro-heating storage device: 21 – adsorbent, 24 – condenser, 28 – water tank, 29 – valve, 30 – container, 31 – evaporator and 32 – liquefier [99].



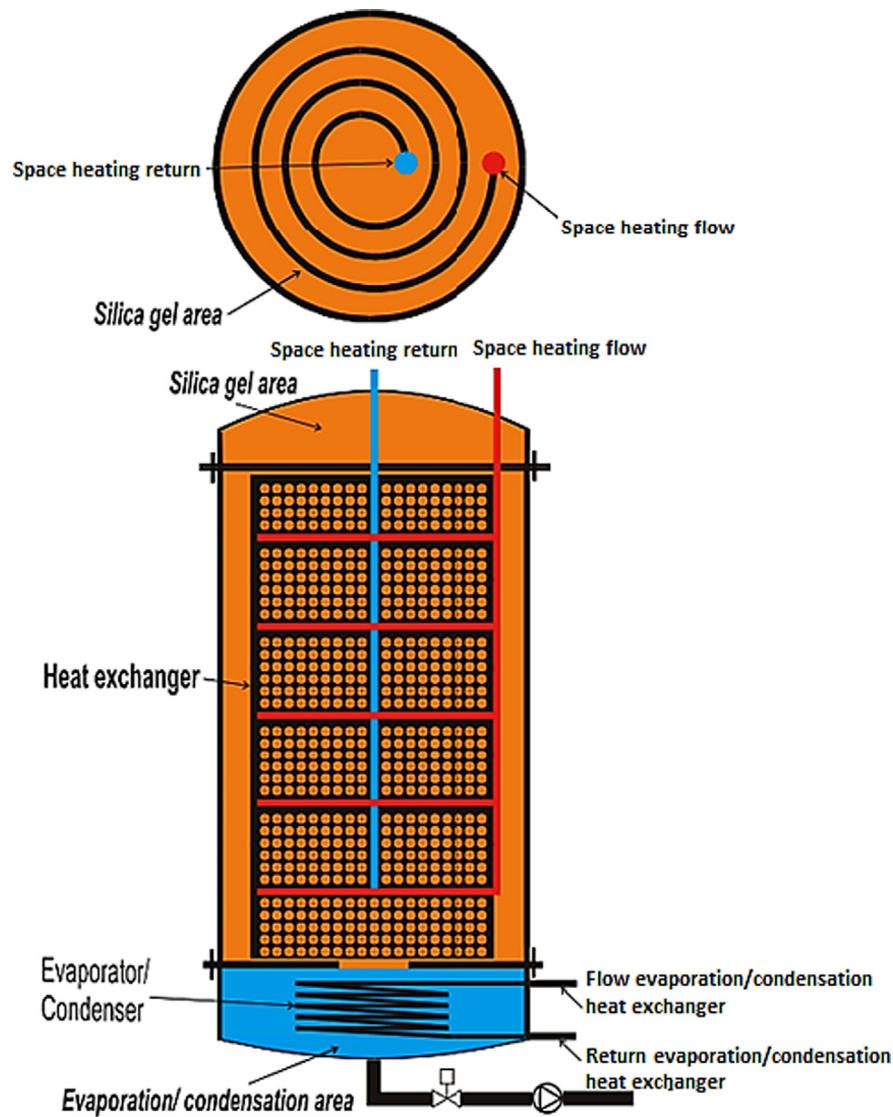


Fig. 22. Compact adsorption thermal storage [100].

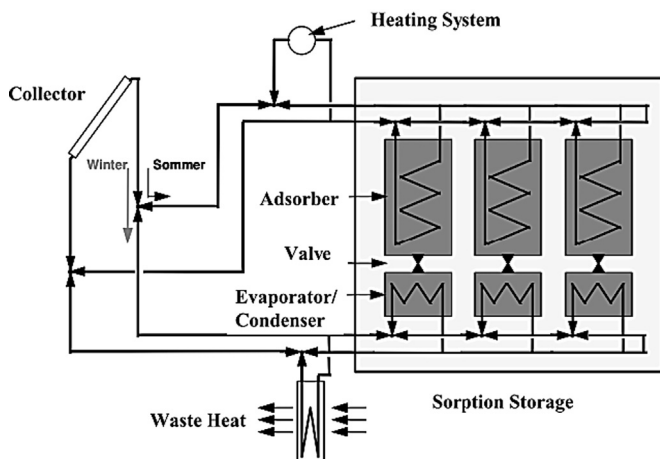


Fig. 23. Seasonal adsorption thermal storage system [102].

Hauer [102] presented a seasonal adsorption thermal energy storage system, operating with silica-gel and water (Fig. 23). During the summer, while the system is charging, the heat from the solar collectors is conducted to three adsorbent beds,

promoting the desorption stage. In the winter, the low temperatures in the solar collector promote the evaporation of the water in the evaporators/condensers, and the heat of adsorption is released to the building heating system. A very similar system was tested in Austria, also providing domestic hot water as well as air heating [102]. This system, which makes use of the silica-gel–water pair, comprises two adsorbers, an evaporator/condenser and a thermal solar plant with an aperture area of 20.4 m<sup>2</sup>. There are two heat sinks to release the condensation heat: a rain water cistern and the thermal solar plant. Thus, desorption and condensation may or may not occur simultaneously. In the former case, the condensation heat is rejected via the rain water cistern. In the latter case, when the desorption and condensation operations are referred as discontinuous, the solar plant heats up the adsorber during daytime but no condensation occurs. The condensation takes place through the solar system during the night, given the correspondingly low outside temperatures. However, the experimental results indicated a 20% lower storage capacity (150 kWh/m<sup>3</sup>) relatively to the simulated results.

Schwamberger et al. [103] performed a simulation study of a novel cycle concept for adsorption heat pumps (“Stratisorp”), operating with the zeolite–water pair (Fig. 24). This cycle makes use of a stratified thermal energy storage to improve the internal

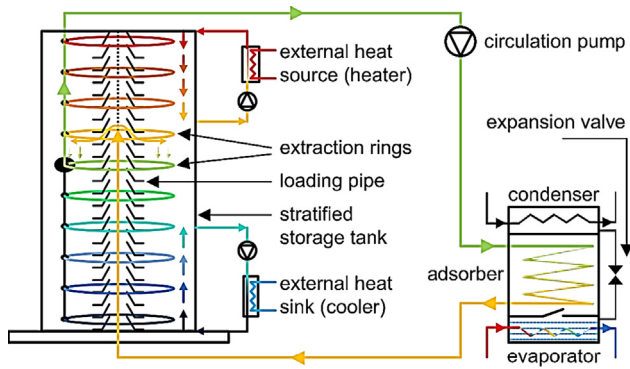


Fig. 24. Stratisorp system [103].

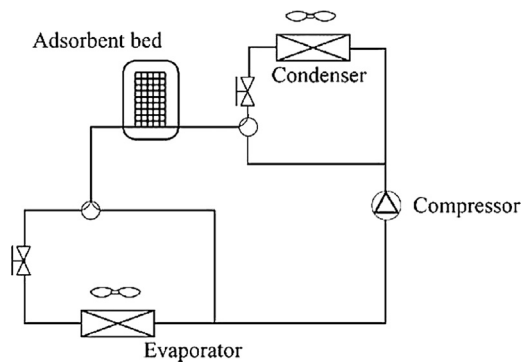


Fig. 25. Hybrid compression and adsorption refrigeration cycle [104].

heat recovery between the adsorption and desorption phases of the cycle. During the adsorption phase, the heat of adsorption is carried away by cooler heat transfer fluid from the adsorber to the storage tank, entering at a height corresponding to its temperature. During the desorption phase, the adsorber is heated by supplying warm fluid from the storage tank, while the cooler fluid returning from the adsorber is stored in the storage tank. An external heat source helps to preserve the stratification effect in the tank. The heat rejected in the condenser and in an external heat sink can be used for room heating. Another possible configuration is placing the stratified storage tank within a DHW tank, so that the rejected heat is transferred to the external DHW tank. The authors reported that the results regarding the system's COP and the recoverable heat are quite significant for further developments.

#### 4.3. Combination with other refrigeration cycles

It is also possible to combine the basic adsorption refrigeration cycle with other refrigeration cycles in order to increase the overall performance. Several research projects have been devoted to this subject. In 1999, Inoue and Honda [104] patented in Japan a refrigeration unit combining the adsorption and the vapor compression refrigeration cycles, to achieve a higher cooling effect (Fig. 25). The unit is provided with a compressor, a condenser, an evaporator and an adsorbent bed. The adsorbent generates heat during the adsorption phase and absorbs heat during the desorption phase. During the cooling phase, the refrigerant discharged from the compressor flows to the adsorbent bed, instead of the condenser, releasing the adsorbate from the adsorbent to be condensed. During the non-cooling phase, the adsorbent bed is cooled by the condensed refrigerant from the condenser, promoting the adsorption phase.

In 2002, a continuous combined solid adsorption–ejector refrigeration and heating hybrid system driven by solar energy,

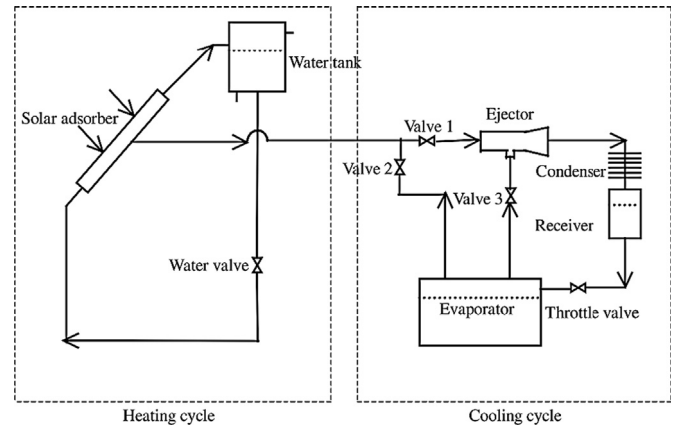


Fig. 26. Continuous solar combined solid adsorption – ejector refrigeration and heating hybrid system [105].

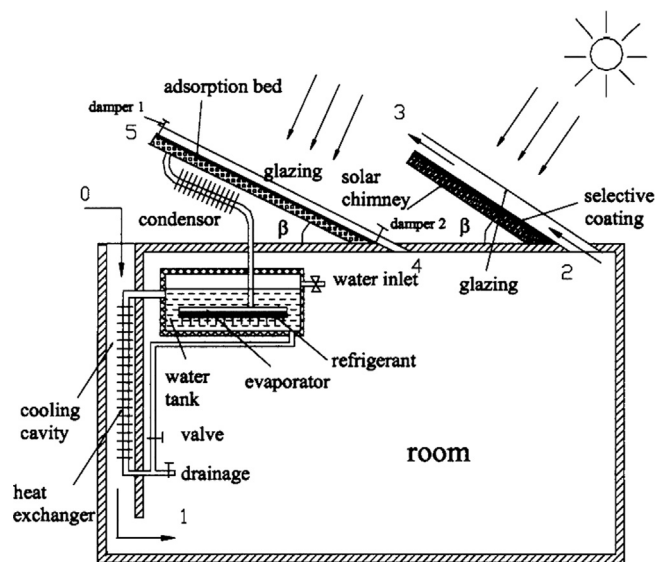


Fig. 27. Solar house with solar chimney and adsorption cooling cavity [106].

operating with the zeolite–water working pair, was presented by Zhang and Wang [105]. The combined system consists of two parts: a heating cycle and a cooling cycle, as shown in Fig. 26. The solar collector consists of a 2 m<sup>2</sup> CPC collector. During daytime, the adsorber receives solar energy and releases the water vapor from the zeolite. Then the adsorber is connected to the ejector and disconnected from the evaporator. The water vapor is then ejected at a fast speed in the ejector, creating a low pressure area, into which water vapor from the evaporator is pulled. The mixed water vapor is compressed into the condenser by the diffuser, the liquid enters to the receiver, and finally returns to the evaporator by the throttle valve. In the afternoon, the adsorber is disconnected from the ejector and connected to the evaporator. Thus, the cold water in the tank circulates into the adsorber to be heated, thus cooling the adsorber. The hot water collected in the tank can then be used for domestic applications in the evening. When the adsorber's temperature and pressure decrease to the evaporation state, evaporation starts in the evaporator. So the system will refrigerate continuously. From the simulation results, the combined hybrid system had a total cooling capacity of 0.49 MJ per kg of zeolite with a COP of 0.33, and could deliver 290 kg of hot water at 45 °C with a heating COP of 0.55.

Also in China, Dai et al. [106] presented a parametric analytical study on the enhancement of natural ventilation in a solar house



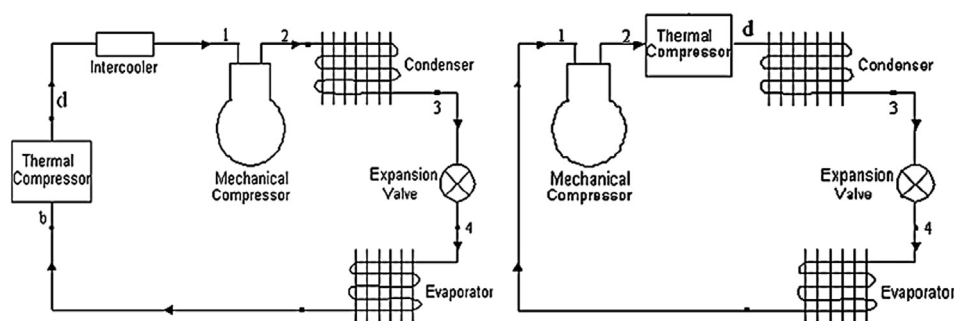


Fig. 28. Hybrid refrigeration system: left side – low stage thermal compression; right side – high stage thermal compression [108].

induced by a solar chimney and a solid adsorption cooling cavity. In this system (Fig. 27), a water tank is cooled by the adsorption effect during the night. During daytime, the solar energy heats up the air in a solar chimney, and a cooling cavity cools down the air (through the cold effect provided by the water tank), in order to induce ventilation in the room: the hot air moves upwards, while the cold air moves down. At night, ventilation is induced mainly by the heat storage in the solar chimney. It is found that on a typical day, the solar house comprising of a 2.5 m solar chimney is able to create an airflow rate of more than 150 kg/h. The solar COP could reach a value of 0.12.

In Japan, Kakiuchi et al. [107] invented a hybrid adsorption and vapor compression heat pump to improve the overall COP. The heat pump main cycle comprises a compressor, a condenser and an evaporator. An adsorption type cooling device is included in the system. The adsorbent bed makes use of the condensation heat of the vapor compression system to promote the desorption effect.

Banker et al. [108] studied the performance of adsorption and mechanical hybrid compression refrigeration cycles operating with HFC 134a. The mechanical compression effect is supplemented by thermal compression (string of adsorbers). The refrigerant is conducted from the evaporator into the thermal compressor (low stage compression), where it is adsorbed by activated carbon. Subsequently, desorption is promoted by a heat source, and the resulting refrigerant vapor is conducted to an intercooler and then into a mechanical compressor, where the high stage compression occurs (Fig. 28 – left side). Another possibility is to use the mechanical compressor for the low stage compression (Fig. 28 – right side). This study shows that it is possible to save almost 40% of energy by carrying out a part of the compression in a thermal compressor in comparison to the use of a single-stage mechanical compressor.

## 5. Conclusions

This paper presents an extensive review of the state of the art of solar refrigeration systems operating with the basic adsorption cycle. The operation principle is explained, covering its main components, thermodynamic aspects and performance assessment. The most commonly used adsorbate–adsorbent working pairs are also described, presenting some specific requirements, advantages and disadvantages in their selection.

The intermittent solar adsorption refrigeration system has been extensively studied both theoretically and experimentally, mainly due to its simplicity and low operation costs. This kind of adsorption system has several advantages over the common vapor compression refrigeration systems. The environmental benefits of this technology and its non-dependence on conventional energy sources makes it highly attractive for further developments and a potential alternative to conventional systems in the future.

Furthermore, due to the year-round availability of sunlight, solar energy can be easily captured all over the world.

The literature reveals that solar-powered adsorption refrigeration devices can supply, among others, the needs for refrigeration, air-conditioning applications and ice making, with great potential in the conservation of some goods (e.g., medicines, food supplies) in remote areas. It is also seen that the adsorption systems with flat plate solar collectors and intermittent operations are simpler (and cheaper) than other types, and the most commonly used working pair is activated carbon and methanol. Nevertheless, the purpose of each system (e.g., air-conditioning, ice making) and the ambient conditions dictate its configuration (e.g., type of solar collector) and working pair, and therefore its performance.

However, despite all the efforts made and numerous studies conducted all over the world regarding the improvement of solar adsorption refrigeration systems, over the last decades, a lot of research work still needs to be done in order to further improve its performance (e.g., enhancement of heat and mass transfer, research on adsorbent materials, efficiency of solar collectors) and decrease the investment costs, making this technology competitive. Even with the current technology, the average daily ice production of these machines did not significantly improve, and the experimental solar COP is still considerably low (typically, between 10% and 20%), seeming unlikely of further increase. However, it must be mentioned that the results depend heavily on the solar radiation and ambient temperature under which the systems operate. Furthermore, this kind of systems has very little commercial success, and most of the current applications are in the stage of demonstration and prototyping. In addition, the majority of the tests, even by simulation, have been conducted for specific cases, not being able to predict how the systems will operate under different conditions.

Nevertheless, there are already many research works regarding modified adsorption refrigeration cycles, aiming to improve the efficiency and practicability of the basic intermittent cycle. These include, among others, the heat recovery, mass recovery, thermal wave, multi-bed and multi-stage cycles. However, it is possible to maintain the simplicity of the basic adsorption cycle and take advantage of its operation, and still enhance its performance in other ways.

Recently, many researchers are focused on the development of hybrid adsorption systems, in what it seems to be a new research trend. An overview of the hybrid adsorption systems operating with the basic cycle has also been conducted in this paper, to understand its present status and future trends. Combined systems of solar adsorption cooling and heating improve the overall system performance by recovering the condensation heat and/or the heat of adsorption to produce hot water. Another possibility is to use the adsorption systems as thermal energy storage devices, allowing for long-term heat or cold storage without losses. On the other hand, combining the adsorption cycle with other refrigeration cycles also improves the overall performance of the system

and the cooling production. In this field, the biggest potential seems to come from the adsorption thermal storage systems, due to their capacity to store thermal energy for long periods of time without losses, allowing for better use of the energy available at each instant and thus for major energy savings. In turn, the adsorption systems which recover the condensation and/or adsorption heat also present great advantages when correctly applied (e.g., DHW and ice production).

These research options extend the area of applications of adsorption technologies and make the solar adsorption systems much more attractive and cost effective. However, further studies still need to be carried out to develop these technologies and to validate their potential for future commercial applications, in order to replace, or at least to integrate, the current non-environmentally friendly systems. The next few years will be decisive for the success of these adsorption systems, depending on proper energy directives, as well as the efforts undertaken by the researchers and manufacturers in this area.

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